THE NATURAL STATES OF THE BERYLLIUM ATOM

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CHAPTER I

INTRODUCTION

Progress in the quantum theory of many body systems has for many years been extremely slow because of the difficulty of calculating accurate wave functions for systems of more than two fermions. A resurgence of interest in many-body quantum theory has recently arisen partly because of the recognition of the importance of density matrices in calculating the properties of these systems (1,2,3). In fact, it is well known that a knowledge of the second order density matrix is sufficient to describe all the properties of a system of N fermions in which only two body interactions are taken into account. For example, the non-relativistic Schrödinger equation for an atom in the stationary-nucleus approximation is

$$\left[\sum_{i=1}^{N} \left(-\frac{\hbar^2 \nabla_i^2}{2m} - \frac{Z e^2}{r_i} \right) + \sum_{i<j} \frac{e^2}{r_{ij}} \right] \Psi = E \Psi \qquad (1.1)$$

and for atoms of low atomic number Z the difference between E and the total experimental energy Eexp is quite small. The difference is due mostly to relativistic effects, which may be estimated.

Density matrices were introduced by von Neumann (4), Dirac (5), and Husimi (6), and their use in Hartree-Fock (7) calculations of

atomic systems investigated by Fock (8) and Lennard-Jones (9). The considerable literature of density matrices is excellently covered in two review articles by McWeeny (2) and ter Haar (10).

Modern developments in the theory of density matrices have centered about the N-representability problem (11), which can be formulated: given a function $f(x_1'x_2'\ldots x_p'|x_1x_2\ldots x_p)$ or f^p, then it is N-representable if an antisymmetric function $\Psi(x_1x_2\ldots x_px_{p+1}\ldots x_N)$ exists such that

$$f^p = \binom{N}{p}\int \Psi\,\Psi^{*\prime}\,dx_{p+1}\cdots dx_N$$

where $\Psi' = \Psi(x_1'x_2'\cdots x_p'\,x_{p+1}\cdots x_N)$.

The function f^p is called the pth order density matrix, and the first order density matrix for He and H_2 has been calculated (12,13), and necessary and sufficient conditions have been obtained by Coleman (11) for the first order density matrix to be N-representable.

The problem remains to find the conditions for the N-representability of the second order density matrix. To date, however, no second order density matrix has been calculated for wave functions more accurate than Hartree-Fock wave functions, and Löwdin (14) has shown that the first order density matrix in the Hartree-Fock scheme, where the wave function is approximated by a single Slater determinant, determines all higher-order density matrices.

The purpose of this investigation is to determine the second order density matrix for a wave function more accurate than that approximated by a single Slater determinant. The method and normalization used will be that given by Löwdin (1) which is familiar

to chemists. Watson's (15) wave function for the beryllium atom is used for the calculation.

Carlson and Keller (16) have shown how the wave function can be expanded in terms of the eigenfunctions and eigenvalues of the density matrices. This enables one to analyze the wave function in terms of the eigenfunctions and eigenvalues of the density matiix. Specifically the eigenvalue of the second order density matrix may be interpreted as the occupancy number of the corresponding eigenfunction.

In Chapter II, we review the theory of density matrices. Chapter III is devoted to obtaining the correct ^1S wave function by the projection operator technique. Since Watson published only the starting configurations with their associated normalized coefficients, it was necessary to project out the particular ^1S state that he specified to obtain the precise form of the desired wave function.

Chapter IV exhibits the calculation of the first order density matrix. The matrix is diagonalized so that eigenfunctions, called the natural spin orbitals (NSO's) by Löwdin, are obtained with their associated eigenvalues. In this chapter we discuss the expansion of the wave function in terms of products of one and three particle functions according to the Carlson-Keller duality theorem (16). The calculation of the first order density matrix was done by hand, and diagonalized on the Alwac III computer in Uppsala through the kindness of Klaus Appel.

Chapter V contains the second order density matrix. A general program for the IBM 709 to calculate the second order density matrix was developed to obtain this matrix. The second order density

matrix is examined in detail and the expansion in products of two particle functions is obtained. These two-particle functions were named geminals by Harrison Shull (17).

The last two chapters contain a discussion of results and conclusions, (Chapter VI) and the summary (Chapter VII).

While this work was in progress, Weiss (38) and Kelley (39) reported calculations of the ground state energy E of the Be atom. Weiss with a 55 configuration wave function found that E = -14.66090 a.u. Kelley (39) used Goldstone's perturbation theory to find E = -14.66311 a.u. These results may be compared with the lowest eigenvalue of the Schrödinger equation (1.1), as estimated from spectroscopic data (45), corrected relativistically (46), to give -14.6662 a.u. Watson (15) obtained a more accurate result by using spectroscopic data to obtain the first two ionization potentials for Be, and then using Pekeris' calculations (47) for the nonrelativistic energy of Be^{++}. The result was E_{exact} = -14.66745 a.u. Watson's calculated energy was E = -14.6574 a.u.

CHAPTER II

REVIEW OF DENSITY MATRIX THEORY

The Natural Expansion

Given an antisymmetric wave function $\Psi(x_1 \cdots x_N)$, assumed to be normalized to unity for a system of N-indistinguishable fermions, one may define the pth order density matrix as

$$D^p(x_1 \cdots x_p ; x_1' \cdots x_p') = \binom{N}{p} \int \Psi(x_1 \cdots x_p\, x_{p+1} \cdots x_N) \Psi^*(x_1' \cdots x_p' x_{p+1} \cdots x_N)\, dx_{p+1}\, dx_{p+2} \cdots dx_N \quad (2.1)$$

where x_i is the space and spin coordinate of the ith particle. It is convenient to label the coordinates $x_1 x_2 \cdots x_p$ as the p-particles and the coordinates $x_{p+1} \cdots x_N$ as the q-particles. Thus to indicate integration over the space of functions of the p and q particles we write

$$\int f_1^p{}^*(\mathfrak{s}) f_2^p(\mathfrak{s})\, d\mathfrak{s} \qquad \text{and} \qquad \int f_1^q{}^*(\mathfrak{t}) f_2^q(\mathfrak{t})\, d\mathfrak{t}$$

respectively. These shorthand formulae enable us to condense the notation so that $\mathfrak{s}$ and $\mathfrak{t}$ refer to the points in the p- and q-particle space respectively, and $d\mathfrak{s}$ and $d\mathfrak{t}$ are the approximate differentials. Formula (2.1) now becomes

$$D^p(\mathfrak{s}, \mathfrak{s}') = \binom{N}{p} \int \Psi(\mathfrak{s}, \mathfrak{t})\, \Psi^*(\mathfrak{s}', \mathfrak{t})\, d\mathfrak{t} \quad (2.2)$$

and we have the analogous formula

$$D^q(x,x') = \binom{N}{q} \int \Psi(\lambda, x)\, \Psi^*(\lambda, x')\, d\lambda \quad . \tag{2.3}$$

We may regard the wave function $\Psi(\lambda,x)$ as the kernel of linear integral operators Ψ^p_q and Ψ^q_p in the Hilbert space of square integrable functions of p and q variables, so that we may write

$$\Psi^q_p f^p(x) = \int f^p(\lambda)\, \Psi(\lambda, x)\, d\lambda \tag{2.4}$$

$$\Psi^p_q f^q(\lambda) = \int \Psi(\lambda, x) f^q(x)\, dx \tag{2.5}$$

Originally f^p and f^q were functions on the p and q space respectively, but by operating on them with

$$\Psi^q_p = \int \Psi(\lambda, x)\, d\lambda \qquad \text{and} \qquad \Psi^p_q = \int \Psi(\lambda, x)\, dx$$

we get functions $\Psi^q_p f^p(x) = g^q(x)$ and $\Psi^p_q f^q(\lambda) = g^p(\lambda)$.

We note that the scalar product is defined as

$$\langle f^p, g^p \rangle = \int f^p\, g^{p*}\, d\lambda \quad . \tag{2.6}$$

Due to the antisymmetry of the Ψ functions it can easily be shown that $D^p(\lambda,\lambda')$ and $D^q(x,x')$ are antisymmetric in either set of variables. Also taking the complex conjugate, we find

$$D^q(x,x') = D^{q*}(x',x) \qquad \text{and} \qquad D^p(\lambda,\lambda') = D^{p*}(\lambda',\lambda) \quad .$$

The operators D^p and D^q may be expressed as

$$D^p = \binom{N}{p} \Psi^p_q \Psi^{q*}_p \tag{2.7}$$

$$D^q = \binom{N}{q} \Psi^q_p \Psi^{p*}_q \quad . \tag{2.8}$$

We have the convention that the complex conjugate operator Ψ^{x*}_y has the variables indicated by its lower indices primed in the kernel. Thus the expression $\binom{N}{p} \Psi^p_q \Psi^{q*}_p$ has as its kernel

$$\binom{N}{p} \int \Psi(\lambda, x)\, \Psi^*(\lambda', x)\, d\lambda$$

which checks with formula (2.7). We may check (2.8) in a similar manner. We define the norm $\|f^p\|$ by $\|f^p\| = \langle f^p, f^p \rangle$.

Calculating the quantity $\langle D^p f^p, f^p \rangle$ we find

$$D^p f^p = \binom{N}{p} \Psi_p^p \Psi_p^{p\,*} \{ f^p(\lambda) \} = \int \Psi(\lambda, x) f^p(\lambda') \Psi^*(\lambda', x)\, d\lambda'\, dx$$

and

$$\langle D^p f^p, f^p \rangle = \binom{N}{p} \int f^{p\,*}(\lambda)\ \Psi(\lambda, x) f^p(\lambda')\ \Psi^*(\lambda', x)\, d\lambda\, d\lambda'\, dx$$

$$= \binom{N}{p} \langle \Psi_p^{p\,*} f^p(x)\ ,\ \Psi_p^{p\,*} f^p(x) \rangle \geq 0 .$$

The trace of D^p is written $\mathrm{Tr} D^p = \int D^p(\lambda, \lambda)\, d\lambda = \binom{N}{p}$.

Thus D^p and similarly D^q are positive-semidefinite Hermitian operators with finite trace. This type of operator has a purely discrete spectrum of eigenvalues and its eigenfunctions comprise a complete orthonormal set (18). The elements of this set will be denoted

$$g_i^p(\lambda)\ ,\ i = 1, 2, \cdots$$

or

$$\mathcal{Y}_i^q(x)\ ,\ i = 1, 2, \cdots$$

for the operators D^p and D^q respectively. Thus the theory of integral operators (19) allows us to write the spectral representation as

$$D^p(\lambda, \lambda') = \sum_{i=1}^{\infty} N_i^p\, g_i^p(\lambda)\, g_i^{p\,*}(\lambda')\ ,\quad D^p g_i^p = N_i^p g_i^p .$$

Similarly we may write (16)

$$D^q(x, x') = \sum_{i=1}^{\infty} N_i^q\, \mathcal{Y}_i^q(x)\, \mathcal{Y}_i^{q\,*}(x')\ ,\quad D^q \mathcal{Y}_i^q = N_i^q \mathcal{Y}_i^q$$

and

$$\Psi(\lambda, x) = \binom{N}{p}^{-1/2} \sum_{i=1}^{\infty} (N_i^p)^{1/2}\, g_i^p(\lambda)\, \mathcal{Y}_i^q(x) . \qquad (2.9)$$

We may assume that the eigenvalues N_λ^p can be ordered in such a way that

$$N_1^p \geq N_2^p \geq N_3^p \cdots$$

We note that since D^p and D^q are positive-semidefinite,

$$N_\lambda^q \geq 0 \quad \text{and} \quad N_\lambda^p \geq 0 .$$

Carlson and Keller (16) noticed that $N_\lambda^p = N_\lambda^q$. The g_λ^p and $\mathcal{G}_\lambda^q$ are called the natural p and q states respectively and the number of non-vanishing N_λ^p is called the p-rank of D^p . The Carlson-Keller theorem indicates that the p-rank equals the q-rank.

The importance of the natural states lies in the fact that $\Psi(1,2)$ can only be approximated in most cases. Thus if we wish to find the minimum of

$$\Delta = \| \Psi(1,2) - \sum a_{ij} f_i(1) g_j(2) \|$$

where the sum is taken over $1 \leq i \leq a$, $1 \leq j \leq b$, $a \leq b$ (finite) , and $f_i(1)$, $g_j(2)$ are linearly independent square integrable functions, then the minimum is obtained if we put $a_{ij} = \begin{cases} \kappa_i \delta_{ij} , & j \leq a \\ 0 , & j > a \end{cases}$ and choose

$$f_\lambda(1) = g_\lambda^p(1) , \quad g_\lambda(2) = \mathcal{G}_\lambda^q(2) , \quad \kappa_\lambda = \binom{N}{p}^{-1/2} \left(N_\lambda^p\right)^{1/2} .$$

Thus the best least squares approximation to Ψ as a sum of products of the form $f_\lambda(1) g_\lambda(2)$ is $\binom{N}{p}^{-1/2} \sum_{\lambda=1}^{a} \left(N_\lambda^p\right)^{1/2} g_\lambda^p(1) \mathcal{G}_\lambda^q(2)$.

The proof of this theorem can be found in reference (11).

Upper Bounds to the Occupation Numbers

Sasaki (20) has shown that the best possible upper bound to N_λ^2 is $N/2$ for even N and $(N-1)/2$ for odd N , and it is well known that 1 is the best possible upper bound to N_λ^1 . A theorem by

Coleman (11) establishes upper bounds to N_x^p , $p > 2$; but he did not prove that these bounds were the best possible.

The Density Matrices in k Space

The formula that is used for the calculation (1) of the first and second order density matrices in k space is

$$D^p(l_1 l_2 \cdots l_p | k_1 k_2 \cdots k_p) = \sum_K^{(k_1 k_2 \cdots k_p)} \sum_L^{(l_1 l_2 \cdots l_p)} (-1)^{k_1+k_2+\cdots k_p+l_1+\cdots+l_p} C_K^* D_{KL} (k_1 k_2 \cdots k_p | l_1 l_2 \cdots l_p) C_L / \sum_K |C_K|^2 .$$

This formula reduces to

$$D^1(l|k) = \sum_K^{(k)} \sum_L^{(l)} (-1)^{k+l} C_K^* D_{KL} (k|l) C_L / \sum_K |C_K|^2 \qquad (2.10)$$

and

$$D^2(l_1 l_2 | k_1 k_2) = \sum_K^{(k_1 k_2)} \sum_L^{(l_1 l_2)} (-1)^{k_1+k_2+l_1+l_2} C_K^* D_{KL} (k_1 k_2 | l_1 l_2) C_L / \sum_K |C_K|^2 \qquad (2.11)$$

for the first and second order density matrices respectively. The respective diagonal elements are

$$D^1(k|k) = D^1(k) = \sum_K^{(k)} |C_K|^2 / \sum_K |C_K|^2 \qquad (2.12)$$

$$D^2(k_1 k_2 | k_1 k_2) = D^2(k_1 k_2) = \sum_K^{(k_1 k_2)} |C_K|^2 / \sum_K |C_K|^2 . \qquad (2.13)$$

The notation $\sum_K^{(k)}$ means the sum over all ordered configurations K containing the kth spin orbital. Similarly, $\sum_K^{(k_1 k_2)}$ means the sum over all ordered configurations K containing the pair of spin orbitals $k_1 k_2$ where $k_1 < k_2$. These formulae were derived by expressing the wave function as a sum over a series of ordered Slater determinants $\Psi = \sum_K C_K \Psi_K$ where

$$C_K = C(k_1 k_2 \cdots k_N) \; , \; k_1 < k_2 < \cdots < k_N$$

and

$$\Psi_K(x_1, x_2 \cdots x_N) = (N!)^{-1/2} \det\{\psi_{k_1}, \psi_{k_2} \cdots \psi_{k_N}\} .$$

The $D_{KL}(k_1 k_2 \cdots k_p | l_1 l_2 \cdots l_p)$ are the pth order minors obtained from

$$\int \Psi_K^* \Psi_L \, dx_1 \, dx_2 \cdots dx_N = \det\{d_{KL}(kl)\} = D_{KL}$$

where

$$d_{KL}(kl) = \int \psi_k^*(x_1) \psi_l(x_1) \, dx_1 .$$

Since Watson's wave function is built up from an orthonormal set of functions $(\psi_{k_1}, \psi_{k_2}, \cdots \psi_{k_{1N}})$, $d_{KL}(kl) = \delta_{kl}$ where δ_{ij} is the Kronecker delta function. Therefore each determinant D_{KL} can only have as elements zeroes and ones, and there can be no more than four ones in the determinant. Considering the first order density matrix, we say that two determinants Ψ_K and Ψ_L mix in the first order if there are three or more ones in D_{KL}. This terminology arises from the fact that the ones in the D_{KL} are situated so that rearranging rows or columns will bring the D_{KL} to diagonal form with anywhere from four to no ones in the diagonal and zeroes elsewhere including the missing ones in the diagonal. It is easy to see that the minors $D_{KL}(k|l)$ vanish if D_{KL} has less than three ones in it. Thus those minors $D_{KL}(k|l)$ arising from Ψ_K and Ψ_L which do not mix will not be present in equation (2.10). Similarly we say that for the second order density matrix Ψ_K and Ψ_L do not mix in the second order if D_{KL} has less than two ones in it. It is evident that equation (2.11) contains more terms than equation (2.10). The extra terms in equation (2.11) arise from the one minor obtainable from the D_{KL} containing two ones, and the D_{KL} containing only

two ones arises from the determinants Ψ_K and Ψ_L which do not mix in the first order. Thus the elements of the second order density matrix consist of a sum over more terms than that of the first order density matrix derived from the same wave function.

The functions $g^{\rho}_{\lambda}(1)$ and $\mathcal{G}^{\beta}_{\lambda}(2)$ of equation (2.9) are determined to within a phase factor, and it is necessary to associate $g^{\rho}_{\lambda}(1)$ and $\mathcal{G}^{\beta}_{\lambda}(2)$ by the formula

$$\int g^{\rho *}_{\lambda}(1)\,\Psi(1,2)\,d1 = \left\{N^{\rho}_{\lambda}/\binom{N}{p}\right\}^{1/2}\mathcal{G}^{\beta}_{\lambda}(2) \qquad (2.14)$$

which implies

$$\int \Psi(1,2)\,\mathcal{G}^{\beta *}_{\lambda}(2)\,d2 = \left\{N^{\rho}_{\lambda}/\binom{N}{p}\right\}^{1/2} g^{\rho}_{\lambda}(1). \qquad (2.15)$$

These equations are referred to as the Schmidt (21) phase convention.

The elements N^1_λ and N^2_λ may be interpreted as follows: N^1_λ = number of particles $\times$ the probability of finding the particle in spin orbital $g^1_\lambda(1)$ when all the other particles occupy arbitrary spin orbitals; N^2_λ = number of pairs $\times$ the probability of finding the pair in geminal $g^2_\lambda(1,2)$ when all other particles may occupy arbitrary geminals. The occupancy number in the first case is then $4^{-1}N^1_\lambda$ and in the second case $6^{-1}N^2_\lambda$ for the Be atom.

CHAPTER III

PROJECTION OF THE ^1S COMPONENT OF THE Be WAVE FUNCTION

Projection Operators

The projection operator formalism developed by Löwdin (23,24,25) depends on the fact that an arbitrary trial function for the total system must be resolvable uniquely into orthonormal components of pure angular momentum M associated with different quantum numbers. Unless otherwise indicated all derivations of formulae in this chapter will be found in references (22-26). Our treatment of projection operators is an application of the method of Fieschi and Löwdin (22).

A projection operator or projector is defined as an idempotent $P^2 = P$ and Hermitian $P^\dagger = P$ operator. We are interested in the projection operators which give us the component $\Psi_{k,m}$ of Ψ having a pure angular momentum with the quantum numbers k and m. The quantum number k is related to the operator $\mathcal{M}^2$ by the equation $\mathcal{M}^2 \Psi_{k,m} = k(k+1)\, \Psi_{k,m}$ in units where $\hbar = 1$, so that we may write

$$\{\mathcal{M}^2 - k(k+1)\} \Psi_{k,m} \equiv 0 . \qquad (3.1)$$

Similarly the eigenvalue equation for m is written

$$\{M_z - m\}\,\Psi_{k,m} \equiv 0 . \qquad (3.2)$$

The function $\Psi_{k,m}$ is therefore an eigenfunction to M^2 and M_z with eigenvalues $k(k+1)$ and m respectively. The eigenvalues are related by the equation $m = k, k-1, \cdots, 0, -1, -2, \cdots, -k$ for fixed k, giving the multiplicity $2k+1$. The quantum number k may be either an integer or half integer for spin angular momentum, but is restricted to an integer for orbital angular momentum. We refer to Edmond's book (26) for the conventional theory of angular momentum.

We are interested in projection operators which commute with the Hamiltonian $\mathcal{H}$ so we may write

$$\mathcal{O}\,\mathcal{H} = \mathcal{H}\,\mathcal{O} .$$

An equation which illustrates the power of the projection operators is

$$\int (\mathcal{O}\Phi)^*\,\mathcal{H}\,(\mathcal{O}\Phi)\,d\tau = \int \Phi^*\,\mathcal{H}\,(\mathcal{O}\Phi)\,d\tau .$$

This equation is easily obtained by using the "turn-over rule", the commutability of $\mathcal{O}$ with $\mathcal{H}$, and the fact that $\mathcal{O}^+ = \mathcal{O}$.

In the equation $M^2\,\Psi_{k,m} = k(k+1)\,\Psi_{k,m}$ the values k are determined by the addition theorem for angular momentum (26). For two particles we have $k_1 \geq k_2 \geq 0$, and

$$k = k_1 + k_2 ,\ k_1 + k_2 - 1 ,\ k_1 + k_2 - 2 ,\ \cdots ,\ |k_1 - k_2| .$$

For n particles we have $k_1 \geq k_2 \geq \cdots k_n \geq 0$, and

$$k = k_1 + k_2 + \cdots + k_n ,\ \cdots ,\ \min|k_1 \pm k_2 \pm k_3 \pm \cdots \pm k_n| .$$

The maximum value for k , k_{max} , is obviously the first term in these values.

The normalized step-up and step-down operators can be defined as

$$\mathcal{M}_+ \Psi_{k,m} = \left\{(k-m)(k+m+1)\right\}^{1/2} \Psi_{k,m+1} \qquad (3.3)$$

$$\mathcal{M}_- \Psi_{k,m} = \left\{(k+m)(k-m+1)\right\}^{1/2} \Psi_{k,m-1} \; . \qquad (3.4)$$

The commutation relations between $\mathcal{M}_z$, $\mathcal{M}_+$, $\mathcal{M}_-$ are

$$\mathcal{M}_z \mathcal{M}_+ = \mathcal{M}_+ (\mathcal{M}_z + 1) \qquad (3.5)$$

$$\mathcal{M}_z \mathcal{M}_- = \mathcal{M}_- (\mathcal{M}_z - 1) \qquad (3.6)$$

Also from equations (3.1) and (3.2) we see that $\mathcal{M}^2$ commutes with $\mathcal{M}_z$. Given a function Ψ which consists of a mixture of eigenfunctions $\Psi_{k,m}$ such that $\Psi = \sum C_{k,m} \Psi_{k,m}$ we wish to find the states of pure angular momentum $\Psi_{k,m}$. We can find these states by noting that the operators $\mathcal{M}^2 - k(k+1)$ and $\mathcal{M}_z - m$ kill the component $\Psi_{k,m}$. Thus if we write

$$\mathcal{O}_k(\mathcal{M}^2) = \frac{\mathcal{M}^2 - k_1(k_1+1)}{k(k+1) - k_1(k_1+1)} \times \cdots \times \frac{\mathcal{M}^2 - k_{max}(k_{max}+1)}{k(k+1) - k_{max}(k_{max}+1)} \qquad (3.7)$$

where $k_i \neq k$ and

$$\mathcal{O}_m(\mathcal{M}_z) = \frac{\mathcal{M}_z - m_1}{m - m_1} \times \frac{\mathcal{M}_z - m_2}{m - m_2} \times \cdots \times \frac{\mathcal{M}_z - m_{max}}{m - m_{max}} \qquad (3.8)$$

where $m_i \neq m$, we see that

$$\mathcal{O}_k(M^2)\,\mathcal{O}_m(M_z)\,\Psi = C_{k,m}\,\Psi_{k,m}$$

which is the component with pure angular momentum of quantum numbers k and m. The operator $\mathcal{O}_k = \prod_{l\neq k} \frac{A - a_l}{a_k - a_l}$ where $A\phi_k = a_k\phi_k$ can be proven to be idempotent by noting that

$$\frac{A - a_l}{a_k - a_l} = 1 + \frac{A - a_k}{a_k - a_l}$$

so that $\mathcal{O}_k^2 = \prod_{l\neq k} \frac{A - a_l}{a_k - a_l}$

$$+ \prod_{l\neq k} \frac{(A - a_l)(A - a_k)}{(a_k - a_l)^2} = \mathcal{O}_k .$$

It is evident that $\mathcal{O}_k^\dagger = \mathcal{O}_k$ if A is either self-adjoint or fulfills the condition $AA^\dagger = A^\dagger A$ (a normal operator). In the first case it is obvious that $\mathcal{O}_k^\dagger = \mathcal{O}_k$. The second case has been discussed by Löwdin (24).

Equation (3.7) can be written

$$\mathcal{O}_l(M^2) = \prod_{k\neq l} \frac{M^2 - k(k+1)}{l(l+1) - k(k+1)} \quad . \qquad (3.7a)$$

We can transform this equation by assuming that it operates only on Ψ which are eigenfunctions to M_z with eigenvalue m. This transformation results in very little loss in generality because it is not difficult to construct an eigenfunction to M_z. For example, a determinant constructed from four functions $1s$, $2s$, $3p$, $4p$ will be an eigenfunction to M_z with $m = 0$, if we choose $1s\alpha$, $2s\beta$, $3p_z 1\alpha$, $4p_z 1\beta$ where we have multiplied each function alternately by α and β giving a total of $M_S = 0$ and taken the possible m_l values so that they cancel giving a total $M_L = 0$. We may choose such functions as starting

functions for projecting out the states of pure angular momentum, and, for the sake of simplicity we introduce the condition that $m \geq 0$. The case of the negative m value is then handled by reversing the axis, i.e., substituting $m = -m$. The only possible l values are now $l = m$ to $l = l_{max}$ where l_{max} is evaluated by the addition theorem. Now we are in a position to combine $\mathcal{O}_l$ and $\mathcal{O}_m$ simply by substituting $k+m$ for k, and (3.7a) becomes

$$\mathcal{O}_{lm} = \prod_{k=0,\, k\neq l-m}^{k=k_{max}-m} \frac{\{\mathcal{M}^2 - (k+m)(k+m+1)\}}{\{l(l+1) - (k+m)(k+m+1)\}} \quad . \tag{3.9}$$

The Expanded Form of the Projection Operators

Since we have made the restriction that this operator can only operate on functions Ψ which are eigenfunctions to $\mathcal{M}_z$ with the associated eigenvalue m, we can write (3.9) in the form

$$\mathcal{O}_{lm} = \prod_{k=0,\, k\neq l-m}^{k=k_{max}-m} \frac{\{\mathcal{M}^2 - (\mathcal{M}_z+k)(\mathcal{M}_z+k+1)\}}{(l-m-k)(l+m+k+1)} \quad . \tag{3.10}$$

We can expand (3.10) so that it becomes

$$\mathcal{O}_{lm} = (2l+1)\frac{(l+m)!}{(l-m)!} \sum_{\mu=0}^{l_{max}-l} (-1)^{\mu} \frac{\mathcal{M}_-^{l-m+\mu}\, \mathcal{M}_+^{l-m+\mu}}{\mu!\,(2l+\mu+1)!} \quad . \tag{3.11}$$

A proof of (3.11) will be found in reference (23).

Equation (3.11) was used to project the ^1S state specified by Watson (15). He published the Be atom wave in the form of 37 configurations with normalized coefficients. Each configuration is a combination of four by four Slater determinants Φ_i constructed from an orthonormal basis set of 19 one-electron functions ψ_i.

The Form of the ψ_i Functions

The ψ_i functions were of the form

$$\psi_i(x_a) = [\mu_i(r_a)/r_a]\, S_i(\theta_a \varphi_a) \begin{Bmatrix} \alpha(s_a) \\ \beta(s_a) \end{Bmatrix}$$

where

$$\mu_i = \sum_j C_{ij} \left(\frac{(2Z_j)^{2l+2m_j+3}}{(2l+2m_j+2)!} \right)^{1/2} r^{l+m_j+1} e^{-z_j r}$$

and S_i is a normalized spherical harmonic (with quantum numbers l and m_l). It is to be noted that the μ_i are a normalized linear combination of Slater type radial functions. The values of m_j , the screening constants Z_j , and the coefficients C_{ij} are given in Watson's paper, but will not be introduced here because they are not important for the calculation. The Schmidt process was used by Watson to orthogonalize his basis functions, and he used second order perturbation theory to indicate the most important configurations. However, he found that second or higher order perturbation gave poor estimates of the relative importance of different ^1S configurations, so he constructed the configuration interaction matrix for the most important configurations and then increased the matrix to include additional configurations of uncertain importance to discover the effect of the additions.

Watson states that roughly the first twenty configurations were chosen solely for their importance in improving the Be total energy; the later configurations being chosen partially for their energy contributions and partially for the assistance they gave in answering

questions such as how effective was the choice of the $\psi_i' s$ used in the half-dozen most important configurations. Table 1 exhibits the basis orbitals. The explicit form of the wave function is obtained by specifying for each configuration a "starting function" and its phase. From each "starting function" the ^1S state belonging to that configuration may be obtained by use of the projection operator

$N\, \Theta^L_{00}\, \Theta^S_{00}$, where the factor N is the normalization constant. The phase convention is such that every Slater determinant having all $m_\ell = 0$ has a phase factor of $+1$. Except for certain configurations of type $x^2 y^2$, the "starting function" was the single determinant

$$| \psi_i, 0\alpha \;\; \psi_j, 0\alpha \;\; \psi_k, 0\beta \;\; \psi_\ell, 0\beta | \;,$$

and that for $x^2 y^2$ is described below. Table 2 shows the 37 configuration wave function.

The question arises as to how many linearly independent ^1S functions can be constructed from each configuration. Löwdin (27) has shown a simple combinational method to determine the number of linearly independent functions corresponding to a term $^{2S+1}L(M_L, M_S)$. We will illustrate his method for the configuration $p^2 d^2$. We use the notation

$$p^1, m_\ell \begin{Bmatrix} \alpha \\ \beta \end{Bmatrix} \equiv \begin{Bmatrix} (m_{\ell_i}^i | \\ | m_{\ell_i}^i) \end{Bmatrix} \quad ; \quad p^1, -m_\ell \begin{Bmatrix} \alpha \\ \beta \end{Bmatrix} \equiv \begin{Bmatrix} (\bar{m}_{\ell_i}^i | \\ | \bar{m}_{\ell_i}^i) \end{Bmatrix}.$$

Therefore we can write

$$p^1, 0\alpha \equiv (0_i^i | \qquad p^1, -1\,\alpha \equiv (\bar{1}_i^i |$$

$$p^1, 0\beta \equiv | 0_i^i) \qquad p^1, -1\beta \equiv | \bar{1}_i^i) \;.$$

A typical "starting function" built up from the configuration would become

TABLE 1

LIST OF BASIS ORBITALS ψ_i

i	Orbitals	Alternate Notation Used in Projections (see text)
1	1s	s^1
2	2s	s^2
3	s1	o^1
4	s2	o^2
5	s3	o^3
6	s4	o^4
7	p1	$m_{\ell\ 1}^{\ 1}$
8	p2	$m_{\ell\ 1}^{\ 2}$
9	p3	$m_{\ell\ 1}^{\ 3}$
10	p4	$m_{\ell\ 1}^{\ 4}$
11	p5	$m_{\ell\ 1}^{\ 5}$
12	d1	$m_{\ell\ 2}^{\ 1}$
13	d2	$m_{\ell\ 2}^{\ 2}$
14	d3	$m_{\ell\ 2}^{\ 3}$
15	d4	$m_{\ell\ 2}^{\ 4}$
16	f2	$m_{\ell\ 3}^{\ 2}$
17	f3	$m_{\ell\ 3}^{\ 3}$
18	g2	$m_{\ell\ 4}^{\ 2}$
19	g3	$m_{\ell\ 4}^{\ 3}$

TABLE 2

WATSON'S WAVE FUNCTION $\Psi = \sum_n K_n N_n O_{oo}^{\ell} O_{oo}^{s} \Phi_n$

n	Φ_n	K_n	N_n	n	Φ_n	N_n	K_n
1	$1s^2 2s^2$	0.9575824	1	20	$2s^2 s1s2$	$\sqrt{2}$	0.0102900
2	$1s^2 p1^2$	-0.2844586	$\sqrt{3}$	21	$1s2sp1^2$	$\sqrt{6}$	0.0065906
3	$2s^2 p2^2$	-0.0262111	$\sqrt{3}$	22	$2s^2 g2^2$	$\sqrt{9}$	-0.0008295
4	$2s^2 s2^2$	-0.0232595	1	23	$2s^2 p3p4$	$\sqrt{6}$	0.0000858
5	$2s^2 d2^2$	-0.0059003	$\sqrt{5}$	24	$2s^2 s3s4$	$\sqrt{2}$	-0.0057483
6	$p1^2(^1S)p2^2(^1S)$	0.0070633	3	25	$2s^2 s1s4$	$\sqrt{2}$	-0.0049320
7	$2s^2 p3^2$	-0.0051437	$\sqrt{7}$	26	$2s^2 p2p4$	$\sqrt{6}$	-0.0021912
8	$2s^2 p1p2$	-0.0073743	$\sqrt{6}$	27	$1s^2 p5^2$	$\sqrt{3}$	-0.0008337
9	$p1^2(^1S)s1^2(S)$	0.0056508	$\sqrt{3}$	28	$1s^2 p1p5$	$\sqrt{6}$	0.0013765
10	$1s2ss1^2$	-0.0055013	$\sqrt{2}$	29	$2s^2 d2d3$	$\sqrt{10}$	-0.0015543
11	$1s2sp2^2$	-0.0047417	$\sqrt{6}$	30	$2s^2 f3^2$	$\sqrt{7}$	-0.0004808
12	$2s^2 p2p3$	-0.0051990	$\sqrt{6}$	31	$2s^2 d4^2$	$\sqrt{5}$	-0.0004351
13	$1s^2 d1^2$	-0.0182294	$\sqrt{5}$	32	$p2^2(^1S)d1^2(^1S)$	$\sqrt{15}$	0.0004639
14	$1s2sp1p2$	-0.0062031	3	33	$2s^2 s4^2$	1	0.0020928
15	$2s^2 f2^2$	-0.0018353	$\sqrt{7}$	34	$2s^2 g3^2$	$\sqrt{9}$	-0.0002745
16	$2s^2 s3^2$	0.0003207	1	35	$2s^2 p1^2$	$\sqrt{3}$	-0.0018990
17	$2s^2 d3^2$	-0.0019705	$\sqrt{5}$	36	$1s^2 p1p2$	$\sqrt{6}$	0.0025567
18	$2s^2 p4^2$	-0.0009703	$\sqrt{3}$	37	$1s^2 p2^2$	$\sqrt{3}$	-0.0003084
19	$p1^2(^1S)d2^2(^1S)$	0.0015848	$\sqrt{15}$				

$$(\phi 1, o\alpha \;\; \phi 4, o\alpha \;\; \phi 4, o\beta \;\; \phi 1, o\beta) \equiv (0_1^{\dagger} \, 0_2^{\dagger} \mid 0_2^{\downarrow} \, 0_1^{\downarrow}) \qquad (3.12)$$

The vertical line separates the α and β functions. Classifying the corresponding Slater determinants after the total quantities

$$M_L = \sum_{i=1}^{N} m_\ell(i) \;, \quad M_S = \sum_{i=1}^{N} m_s(i) \;,$$

we can construct a table of the numbers of determinants of different types by first writing down all the possible pairs of ϕ functions and their total M_L values, where we have dropped the upper index since both ϕ's and ϕ's are identical.

Index Number	p Function Pairs	M_L
1	$1_1 1_1$	2
2	$1_1 \overline{1}_1$	0
3	$1_1 0_1$	1
4	$0_1 0_1$	0
5	$\overline{1}_1 \overline{1}_1$	-2
6	$\overline{1}_1 0_1$	-1

Now we write down all the possible pairs of ϕ functions and their total M_L values.

Index Number	d Function Pairs	M_L
1'	$2_2 2_2$	4
2'	$2_2 1_2$	3

continued from page 21

Index Number	d Function Pairs	M_L
3'	$2_2 0_2$	2
4'	$2_2 \bar{1}_2$	1
5'	$2_2 \bar{2}_2$	0
6'	$\bar{2}_2 \bar{2}_2$	-4
7'	$\bar{2}_2 \bar{1}_2$	-3
8'	$\bar{2}_2 0_2$	-2
9'	$1_2 1_2$	2
10'	$1_2 0_2$	1
11'	$1_2 \bar{1}_2$	0
12'	$0_2 0_2$	0
13'	$\bar{1}_2 \bar{1}_2$	-2
14'	$\bar{1}_2 0_2$	-1
15'	$\bar{2}_2 1_2$	-1

For $M_S = 2, -2$; $M_L = 6, -6$ we see that all the determinants are zero because the various combinations that give these values, for example, 1 with $1'$, would have at least two rows the same. For $M_S = 2, -2$, $M_L = 5, -5$ we see that all the determinants are also zero for the same reasons as above.

For $M_S = 2, -2$; $M_L = 4, -4$ we find one non-zero determinant for each value of M_L , M_S :

$$(1, 0_1 2_2 1_2| \ , \ (\bar{2}_2 \bar{1}_2 \bar{1}_1 0_1| \ , \ |1, 0_1 2_2 1_2) \ , \ |\bar{2}_2 \bar{1}_2 \bar{1}_1 0_1) \ .$$

Continuing in this way we can construct a table (Table 3) of the

TABLE 3

NUMBERS OF DETERMINANTS OF DIFFERENT TYPES

M_L \ M_S	2	1	0	-1	-2
6			1		
5		2	4	2	
4	1	6	12	6	1
3	2	13	22	13	2
2	4	20	35	20	4
1	5	27	44	27	5
0	6	29	49	29	6
-1	5	27	44	27	5
-2	4	20	35	20	4
-3	2	13	22	13	2
-4	1	6	12	6	1
-5		2	4	2	
-6			1		

numbers of determinants of different types. The numbers in this table are invarient under a linear transformation which leaves M_L and M_S invarient so that one can resolve the table of numbers into fundamental components and find the possible LS terms. We start at the top, picking the smallest number in the row and subtracting this number from each number in its respective column. The table of numbers that is left after subtractions is then subjected to a repeat process as described above until all numbers vanish. This procedure is illustrated in Table 4.

We note that this simple combinational procedure is quite powerful and gives the degeneracy of each state. The ^1S state of p^2d^2, for example, has a degeneracy of three (the number in parentheses indicates the number of linearly independent functions for that state). In the above, we have assumed the Russel-Saunders (28) coupling for each electron. Atomic angular momentum wave functions for the configurations $d^m p^m$ in the different couplings have been studied by the projection operator technique by Calais and Linderberg (29).

From Table 2 we see that there are two configurations of the type p^2d^2, configurations 19 and 32. In all there are four configurations of the type x^2y^2. Belonging to each configuration x^2y^2 there are, in general, several linearly independent ^1S states. Watson chose that ^1S state belonging to each configuration which had non-zero matrix elements with other configurations used in the calculation. He found that the configurations constructed by combining two electron $(^1S)x^2$ and $(^1S)y^2$ functions had non-zero elements with all the other

TABLE 4

THE RESOLUTION OF THE p^2d^2 CONFIGURATION

| | | |

configurations except the other linearly independent states of the same configuration. Investigating these other linearly independent states, he found that their energy contributions were effectively zero so he didn't use these other states.

In every case where two or more linearly independent ^1S functions could be constructed for a particular configuration, Watson chose that function which gave the largest energy contribution. Furthermore, he set a limit of 6×10^{-5} a.u. (atomic units of energy) for each configuration, and this limit enabled him to choose only one of the linearly independent states for each degenerate configuration.

In each case the starting Slater determinant was represented in the notation of the right-hand side of identity (3.12). After evaluating the function $C_{lm} \Psi$, the final expression can be checked by determining whether it is annihilated by the operator $M^2 - l(l+1)$. In the principal case $m = l$, which holds for the ^1S state, we see from the equation (3.3) that the checking relation becomes $M_+ \{ \mathcal{O}_{00} \Psi \} \equiv 0$, and this last expression is used to check each calculation.

Since $M_+ = \sum_{i=1}^{N} M_+(i)$ we can write

$$M_+ = \sum_{i=1}^{N} M_+(i) \quad , \quad M_- = \sum_{i=1}^{N} M_-(i) \, . \qquad (3.13)$$

Thus the operators M_+^{μ} and M_-^{μ} in equation (3.11) can be expanded in one particle operators which simplifies the calculation.

The normalization constant of the function obtained after projecting is easily obtained by taking the square root of the reciprocal of the coefficient of the leading term in this function.

The proof of this is obtained by introducing an orthonormal set of basis functions ϕ_i, $i = 1 \cdots p$ all having $M_L =$ constant. This set is taken to be complete enough to span the part of Hilbert space, in this case ^1S, under consideration. The ϕ's can be Hartree products or Slater determinants built up from one-particle functions or other basis functions. In the case under consideration in this work they are Slater determinants.

The Normalization Constant

We consider the projected functions $\mathcal{O}\phi_\nu = \sum_{\mu=1}^{p} \phi_\mu C_{\mu\nu}$

The normalization integral is $\int \mathcal{O}^* \phi_\nu^* \mathcal{O} \phi_\nu (d\tau) = N$. Using the turnover rule and the fact that $\mathcal{O}^+ = \mathcal{O}$, $\mathcal{O}^2 = \mathcal{O}$, we find

$$N = \int \phi_\nu^* \mathcal{O} \phi_\nu (d\tau) = C_{\nu\nu} .$$

Remembering that ϕ_ν is the starting function, we see that we can always rearrange $\mathcal{O}\phi_\nu$ so that the leading term is $\phi_\nu C_{\nu\nu}$; thus the normalization constant is $(C_{\nu\nu})^{-1/2}$.

Looking at Table 2 we see that the largest L_{max} occurs in configurations of the type $s^2 g^2$ where $L_{max} = 8$. The projection operator $\mathcal{O}_{00}^L$ is

$$1 - \frac{L_- L_+}{2} + \frac{L_-^2 L_+^2}{12} - \frac{L_-^3 L_+^3}{144} + \frac{L_-^4 L_+^4}{2880} - \frac{L_-^5 L_+^5}{86,400} \cdots + \frac{L_-^8 L_+^8}{8!9!} , \quad L_{max} = 8 .$$

It was evident to the author that when $L_{max} = 8$, the amount of work required to project the ^1S function would be extremely tedious so he decided to find a general formula for the ^1S function of configurations of the type $s^2 l^2$ where $l = 1, 2, 3, 4, \cdots$ corresponding to the spectroscopic symbols $p, d, f, g, \cdots$. In all

the projections we need the coefficients to the step-up and step-down operators. From equation (3.3) we see that they are

$$K^{+}_{l,m_l} = \left\{(l-m_l)(l+m_l+1)\right\}^{1/2} \tag{3.14}$$

$$K^{-}_{l,m_l} = \left\{(l+m_l)(l-m_l+1)\right\}^{1/2} . \tag{3.15}$$

These coefficients are conveniently expressed in Table 5.

We state and prove

Theorem 3.1 If N is the normalization constant then $N=(2l+1)^{-1/2}$ and

$$(^1S)l^2l^2 = N\{(00_l|0_l0)-(01_l|\bar{1}_l0)-(0\bar{1}_l|1_l0)+(02_l|\bar{2}_l0) + (0\bar{2}_l|2_l0)\cdots(-1)^l(0l_l|\bar{l}_l0)+(-1)^l(0\bar{l}_l|l_l0)\} . \tag{3.16}$$

We note that the theorem states only that (3.16) is a singlet S state corresponding to the configuration l^2l^2 .

Proof: The equation (3.16) has $2l+1$ determinants and each determinant has the coefficient $\pm$ one so the normalization factor $(2l+1)^{-1/2}$ is correct. Now for any l , the only determinants which can be a member of the linear combination $N\mathcal{O}^L_{00}\mathcal{O}^S_{00}(00_l|0_l0)$ are the determinants in equation (3.16), for these determinants are the basis functions corresponding to $M_L=0$, $M_S=0$. Thus by showing that the coefficient of each determinant equals $(-1)^k$,

$k=0,1,1,2,2,\cdots$, we prove the theorem.

Let us write (3.16) as

$$c_1(00_l|0_l0)+c_2(01_l|\bar{1}_l0)+c_3(0\bar{1}_l|1_l0)+c_4(02_l|\bar{2}_l0)$$

TABLE 5

THE COEFFICIENTS TO THE STEP-UP AND STEP-DOWN OPERATORS

I / m_I	1/2		1		3/2		2	
	$K+$	K^-	$K+$	K^-	$K+$	K^-	$K+$	K^-
2							0	2
3/2					0	3		
1			0	2			2	6
1/2	0	1			3	2		
0			2	2			6	6
-1/2	1	0			2	3		
-1			2	0			6	2
-3/2					3	0		
-2							2	0

$$+ C_5 (0\,\bar{l}_2 \,|\, 2_2\, 0) + \cdots + C_{2k}(0 k_2 \,|\, \bar{l}_2\, 0) + C_{2k+1}(0\,\bar{k}_2 \,|\, k_2\, 0) + \cdots$$

$$+ C_{2l}(0\, l_2 \,|\, \bar{l}_2\, 0) + C_{2l+1}(0\,\bar{l}_2 \,|\, l_2\, 0) = (^1S)\Lambda^2 l^2 = \mathcal{O}^+_{00}\mathcal{O}^S_{00}(00_2|0_2 0)\,.$$

Since this is the principal case where $L = M_L = 0$, $S = M_S = 0$ we have

$$L + \mathcal{O}^S_{00}\mathcal{O}^L_{00}(00_2|0_2 0) = 0 = K^+_{l,0}C_1(0\,l_2|0_2 0) +$$
$$K^+_{l,-1}C_2(0\,l_2|0_2 0) + K^+_{l,0}C_1(00_2|l_2 0) + K^+_{l,-1}C_3(00_2|l_2 0)$$
$$K^+_{l,1}C_2(0\,2_2|\bar{l}_2 0) + K^+_{l,-2}C_4(00_2|\bar{l}_2 0) + \cdots +$$
$$K^+_{l,k}C_{2k}(0[k+1]_l\,|\,\bar{k}_2\,0) + K^+_{l,-(k+1)}C_{2k+2}(0[k+1]_2\,|\,\bar{k}_2 0)$$
$$+ K^+_{l,k}C_{2k+1}(0\,\bar{k}_2\,|\,[k+1]_2\,0) + K^+_{l,-k}C_{2k+3}(0\,\bar{k}_2\,|[k+1]_2 0)$$
$$+ \cdots + K^+_{l,-1}C_{2l+1}(0[\bar{l}+1]_2\,|\,l_2\,0) =$$

$$\{l(l+1)\}^{1/2}\{C_1 + C_2\}(0\,l_2|0_2 0) + \{l(l+1)\}^{1/2}$$
$$\{C_1 + C_3\}(00_2|l_2 0) + \{(l+2)(l-1)\}^{1/2}\{C_2 + C_4\}(00_2|\bar{l}_2 0)$$
$$+ \{(l+2)(l-1)\}^{1/2}\{C_3 + C_5\}(0\,\bar{l}_2\,|\,2_2\,0) + \cdots +$$
$$(2l)^{1/2}\{C_{2l-1} + C_{2l+1}\}(0[\bar{l}+1]_2\,|\,l_2\,0) = 0\,.$$

In order for this sum to be zero the coefficients must vanish. Thus we get the recursion relations

$$C_1 = -C_2 \qquad C_1 = -C_3$$

$$C_2 = -C_4 \qquad C_3 = -C_5$$

$$C_4 = -C_6 \qquad C_5 = -C_7$$

$$\cdots\cdots\cdots \qquad \cdots\cdots\cdots$$

$$C_{2k} = -C_{2k+2} \qquad C_{2k-1} = -C_{2k+1}$$

$$\cdots\cdots\cdots \qquad \cdots\cdots\cdots$$

$$C_{2l-2} = -C_{2l} \qquad C_{2l-1} = -C_{2l+1}$$

(where we have used $K^+_{l-k} = K^+_{l,(k-1)}$)

which imply $C_1 = -C_2 = -C_3 = C_4 = C_5 = -C_6 = -C_7 = \cdots$.

Setting $C_1 = 1$ completes the proof. Furthermore, we note that any $(^1S)\mathcal{L}^2\mathcal{L}^2$ must be proportional to (3.16). Thus we find

Corollary 3.1 The ^1S function of the configurations of the type $\mathcal{L}^2\mathcal{L}^2$ is non-degenerate.

The Projected Wave Function

The projected wave function is exhibited in Table 6. In this table we use the symbol $\mathcal{O}^S_{oo}$ for the spin angular momentum projector and $\mathcal{O}^L_{oo}$ for the orbital angular momentum projector. In many cases the starting function is already a pure spin state so that it is not necessary to project in spin space. We remind the reader that negative m_l values are indicated by $\overline{m}_l$, and α functions are on the left side of the vertical line whereas β functions are on the right side of the vertical line. The normalization constants are indicated by N_i .

A method for constructing the other linearly independent

functions for configurations which are degenerate has been given by Löwdin (25). To use his method, one starts projecting g functions which can be orthogonalized from the basic set of a degenerate configuration of order g .

The elements of the basic set serve as starting functions, and one hopes that after the g projections one obtains g linearly independent functions. An interesting problem is how one can predict in advance the starting functions which will give linearly independent functions after projecting. This problem is important in the case of a configuration like Ψ_{32} , for here there are fifteen basis functions, whereas the degeneracy is of the order three. Thus of fifteen projected functions only three will be linearly independent.

Can one find these functions without first making all fifteen projections? The answer to this question in the case of Ψ_{32} involves selecting the "best" three starting functions from the basis set. As far as the author knows, no method has yet been discovered to select the "best" starting functions in advance of projecting.

A study of the projected configurations of the type $s^2 x y$ where x and y have the same l value but differ in the radial part reveals:

Theorem 3.2 If N is the normalization constant then $N = (4l+2)^{1/2}$ and

$$(^1S)\, s^2 l_1 l_2 = N\{(00'_l|0^2_l 0) + (00^2_l|0'_l 0) - (0\,1'_l|\bar{1}^2_l 0) - (01^2_l|\bar{1}'_l 0) - (0\,\bar{1}'_l|1^2_l 0) - (0\bar{1}^2_l|1'_l 0) + (02^2_l|2'_l 0) + (02'_l|2^2_l 0) + (0\bar{2}^2_l|2'_l 0) + (0\bar{2}'_l|2^2_l 0) + \cdots + (-1)^l (0\bar{l}'_l|l^2_l 0)\}. \quad (3.17)$$

The proof of this theorem is exactly the same as that of theorem 3.1 and we get

Corollary 3.2 The ^1S function of configurations of the type $s^2 l_1 l_2$ is non-degenerate.

The first and second order density matrices were calculated from the projected ^1S wave function.

In the next chapter we exhibit the first order density matrix and discuss the one-three expansion.

TABLE 6

THE ^1S PROJECTION OF WATSON'S WAVE FUNCTION FOR THE BERYLLIUM ATOM $\Psi = \sum_{n=1}^{37} K_n N_n O^{L}_{oo} O^{S}_{oo} \Phi_n$

$(^1S)\Psi_1 = (1s^2 2s^2) = (s^1 s^2 | s^2 s^1)$, $K_1 = 0.9575824$

$(^1S)\Psi_2 = N_2 O^{L}_{oo}(1s^2 p1^2) = N_2 O^{L}_{oo}(s^1 o_1^1 | o_1^1 s^1) = \frac{1}{\sqrt{3}}\{(s^1 o_1^1 | o_1^1 s^1) -$

$(s^1 1_1^1 | \bar{1}_1^1 s^1) - (s^1 \bar{1}_1^1 | 1_1^1 s^1)\}$, $K_2 = -0.2844586$, $N_2 = \sqrt{3}$

$(^1S)\Psi_3 = N_3 O^{L}_{oo}(2s^2 p2^2) = N_3 O^{L}_{oo}(s^2 o_1^2 | o_1^2 s^2) = \frac{1}{\sqrt{3}}\{(s^2 o_1^2 | o_1^2 s^2) -$

$(s^2 1_1^2 | \bar{1}_1^2 s^2) - (s^2 \bar{1}_1^2 | 1_1^2 s^2)\}$, $K_3 = -.0262111$, $N_3 = \sqrt{3}$

$(^1S)\Psi_4 = (2s^2 s1^2) = (s^2 o^1 | o^1 s^2)$, $K_4 = -0.0232595$

$(^1S)\Psi_5 = N_5 O^{L}_{oo}(2s^2 d2^2) = N_5 O^{L}_{oo}(s^2 o_2^2 | o_2^2 s^2) = \frac{1}{\sqrt{5}}\{(s^2 o_2^2 | o_2^2 s^2) -$

$(s^2 1_2^2 | \bar{1}_2^2 s^2) - (s^2 \bar{1}_2^2 | 1_2^2 s^2) + (s^2 2_2^2 | \bar{2}_2^2 s^2) + (s^2 \bar{2}_2^2 | 2_2^2 s^2)\}$

$K_5 = -0.0059003$, $N_5 = \sqrt{5}$

In this case $\Psi_6 = (p1^2(^1S) \times p2^2(^1S))$. Watson took two ^1S two electron product functions to make the ^1S four electron term, as follows:

$NO^{L}_{oo} p1^2 = \frac{1}{3}\{(o_1^1 | x | o_1^1) - (1_1^1 | x | \bar{1}_1^1) - (\bar{1}_1^1 | x | 1_1^1)\}$

$NO^{L}_{oo} p2^2 = \frac{1}{3}\{(o_1^2 | x | o_1^2) - (1_1^2 | x | \bar{1}_1^2) - (\bar{1}_1^2 | x | 1_1^2)\}$

Antisymmetrizing the product $NO_{oo} p1^2 NO_{oo} p2^2$ we find

TABLE 6 continued

$$({}^1S)\Psi_6 = \frac{1}{3}\{|o_1^1 o_1^2| o_1^2 o_1^1| - |o_1^1 1_1^2| \bar{1}_1^2 o_1^1| - |o_1^1 \bar{1}_1^2| 1_1^2 o_1^1| - |1_1^1 o_1^2| o_1^2 \bar{1}_1^1| +$$
$$|1_1^1 1_1^2| \bar{1}_1^2 1_1^1| + |1_1^1 \bar{1}_1^2| 1_1^2 1_1^1| - |\bar{1}_1^1 o_1^2| o_1^2 1_1^1| + |\bar{1}_1^1 1_1^2| \bar{1}_1^2 1_1^1| +$$
$$|\bar{1}_1^1 \bar{1}_1^2| 1_1^2 1_1^1|\} = N_6 o_{oo}^t p1^2 o_{oo}^t p2^2 \ , \ K_6 = 0.0070633 \ , \ N_6 = 3$$

$$({}^1S)\Psi_7 = N_7 o_{oo}^t (2s^2 p3^2) = N_7 o_{oo}^t (s^2 o_1^3 | o_1^3 s^2) = \frac{1}{\sqrt{3}}\{(s^2 o_1^3 | o_1^3 s^2) -$$
$$(s^2 1_1^3 | \bar{1}_1^3 s^2) - (s^2 \bar{1}_1^3 | 1_1^3 s^2)\} \ , \ K_7 = -0.0051437 \ , \ N_7 = \sqrt{3}$$

$$({}^1S)\Psi_8 = N_8 o_{oo}^t o_{oo}^s (2s^2 p1p2) = N_8 0_{oo} 0_{oo} (s^2 o_1^1 | o_1^2 s^2) = \frac{1}{\sqrt{6}}\{(s^2 o_1^1 | o_1^2 s^2) +$$
$$(s^2 o_1^2 | o_1^1 s^2) - (s^2 1_1^1 | \bar{1}_1^2 s^2) - (s^2 \bar{1}_1^1 | 1_1^2 s^2) -$$
$$(s^2 1_1^2 | \bar{1}_1^1 s^2)\} \ , \ K_8 = -0.007374\overline{3} \ , \ N_8 = \sqrt{6}$$

$$({}^1S)\Psi_9 = AN_9 o_{oo}^t [p1^2] \ [s1^2] = \frac{1}{\sqrt{3}}\{(o_1^1 o^1 | o^1 o_1^1) - (1_1^1 o^1 | o^1 \bar{1}_1^1) -$$
$$(\bar{1}_1^1 o^1 | o^1 1_1^1)\}, \ K_9 = 0.0056508 \ , \text{ where A = the antisymmetrization}$$
$$\text{operator.} \ N_9 = \sqrt{3}$$

$$({}^1S)\Psi_{10} = N_{10} o_{oo}^t (1s2ss1^2) = \frac{1}{\sqrt{2}}\{(s^1 o^1 | o^1 s^2) + (o^1 s^2 | s^1 o^1)\}$$
$$K_{10} = -0.0055013 \ , \ N_{10} = \sqrt{2}$$

$$({}^1S)\Psi_{11} = N_{11} o_{oo}^t o_{oo}^s (1s2sp2^2) = N_{11} o_{oo}^t o_{oo}^s (s^1 o_1^2 | o_1^2 s^2) = \frac{1}{\sqrt{6}}\{(s^1 o_1^2 | o_1^2 s^2) +$$
$$(o_1^2 s^2 | s^1 o_1^2) - (s^1 1_1^2 | \bar{1}_1^2 s^2) - (s^1 \bar{1}_1^2 | 1_1^2 s^2) - (\bar{1}_1^2 s^2 | s^1 1_1^2) -$$
$$(1_1^2 s^2 | s^1 \bar{1}_1^2)\} \ , \ K_{11} = -0.0047417 \ , \ N_{11} = \sqrt{6}$$

TABLE 6 continued

$(^1S)\Psi_{12} = N_{12}0^4_{00}0^5_{00}(2s^2p2p3) = N_{12}0^4_{00}0^5_{00}(s^20^2_1|0^3_1s^2) =$

$\frac{1}{\sqrt{6}}\{(s^20^2_1|0^3_1s^2) + (s^20^3_1|0^2_1s^2) - (s^21^2_1|\bar{1}^3_1s^2) - (s^2\bar{1}^2_1|1^3_1s^2) -$

$(s^2\bar{1}^3_1|1^2_1s^2) - (s^21^3_1|\bar{1}^2_1s^2)\}$, $K_{12} = -0.0051990$, $N_{12} = \sqrt{6}$

$(^1S)\Psi_{13} = N_{12}0^4_{00}(1s^2d1^2) = N_{12}0^4_{00}(s^10^1_2|0^1_2s^1) = \frac{1}{\sqrt{5}}\{(s^10^1_2|0^1_2s^1) -$

$(s^11^1_2|\bar{1}^1_2s^1) - (s^1\bar{1}^1_2|1^1_2s^1) + (s^12^1_2|\bar{2}^1_2s^1) + (s^1\bar{2}^2_2|2^2_2s^1)\}$

$K_{13} = -0.0182294$, $N_{13} = \sqrt{5}$

$(^1S)\Psi_{14} = N_{14}0^4_{00}0^5_{00}(1s2s1p2) = N_{14}0^4_{00}0^5_{00}(s^10^1_1|0^2_1s^2) =$

$\frac{1}{3}\{(s^10^1_1|0^2_1s^2) + (0^2_1s^2|s^10^1_1) + (s^1\bar{1}^1_1|s^21^2_1) + (s^21^2_1|s^11^1_1) +$

$(s^11^1_1|s^2\bar{1}^2_1) + (s^2\bar{1}^2_1|s^11^1_1)\} + \frac{1}{6}\{(0^2_1s^1|s^20^1_1) - (0^1_10^2_1|s^1s^2) -$

$(s^1s^2|0^1_10^2_1) + (0^1_1s^2|s^10^2_1) - (s^11^2_1|\bar{1}^1_1s^2) - (\bar{1}^1_1s^2|s^11^2_1) -$

$(s^11^2_1|\bar{1}^1_1s^2) - (1^1_1s^2|s^1\bar{1}^2_1) + (\bar{1}^1_11^2_1|s^1s^2) + (s^1s^2|\bar{1}^1_11^2_1) +$

$(1^1_1\bar{1}^2_1|s^1s^2) + (s^1s^2|1^1_1\bar{1}^2_1)\}$, $N_{14} = 3$, $K_{14} = -.0062031$

$(^1S)\Psi_{15} = N_{15}0^4_{00}(2s^2f2^2) = N_{15}0^4_{00}(s^20^2_3|0^2_3s^2) = \frac{1}{\sqrt{7}}\{(s^20^2_3|0^2_3s^2) -$

$(s^21^2_3|\bar{1}^2_3s^2) - (s^2\bar{1}^2_3|1^2_3s^2) + (s^22^2_3|2^2_3s^2) + (s^2\bar{2}^2_3|2^2_3s^2) -$

$(s^23^2_3|3^2_3s^2) - (s^23^2_3|3^2_3s^2)\}$, $K_{15} = -0.0018353$, $N_{15} = \sqrt{7}$

$(^1S)\Psi_{16} = (2s^2s3^2) = (s^20^3\ 0^3s^2)$, $K_{16} = 0.0003207$

TABLE 6 continued

$$({}^1S)\Psi_{17} = N_{17}0^t_{oo}(2s^2d3^2) = N_{17}0^t_{oo}(s^2o^3_2|o^3_2s^2) = \frac{1}{\sqrt{5}}\{(s^2o^3_2|o^3_2s^2) - (s^2\overline{1}^3_2|\overline{1}^3_2s^2) - (s^2\overline{1}^3_2|1^3_2s^2) + (s^2\overline{2}^3_2|\overline{2}^3_2s^2) + (s^2\overline{2}^3_2|2^3_2s^2)\}$$

$$K_{17} = -0.0019705 \ , \ N_{17} = \sqrt{5}$$

$$({}^1S)\Psi_{18} = N_{18}0^t_{oo}(2s^2p4^2) = N_{18}0^t_{oo}(s^2o^4_1|o^4_1s^2) = \frac{1}{\sqrt{3}}\{(s^2o^4_1|o^4_1s^2) - (s^2\overline{1}^4_1|\overline{1}^4_1s^2) - (s^2\overline{1}^4_1|1^4_1s^2)\} \ , \ K_{18} = -0.0009703 \ , \ N_{18} = \sqrt{3}$$

$$({}^1S)\Psi_{19} = AN_{15}0^t_{oo}[p1^2]0^t_{oo}[d2^2] = \frac{1}{\sqrt{15}}\{(o^1_1o^2_2|o^2_2o^1_1) - (o^1_1\overline{1}^2_2|\overline{1}^2_2o^1_1) - (o^1_1\overline{2}^2_2|2^2_2o^1_1) + (o^1_2o^2_2|\overline{2}^2_2o^1_1) + (o^1_2\overline{1}^2_2|1^2_2o^1_1) - (1^1_1o^2_2|o^2_1\overline{1}^1_1) + (\overline{1}^1_1\overline{1}^2_2|\overline{1}^2_2\overline{1}^1_1) + (1^1_1\overline{1}^2_2|1^2_2\overline{1}^1_1) - (1^1_1\overline{2}^2_2|\overline{2}^2_2\overline{1}^1_1) - (\overline{1}^1_1o^2_2|o^2_1\overline{1}^1_1) + (\overline{1}^1_1\overline{1}^2_2|\overline{1}^2_2\overline{1}^1_1) + (\overline{1}^1_1\overline{1}^2_2|1^2_2\overline{1}^1_1) - (\overline{1}^1_1\overline{2}^2_2|\overline{2}^2_2\overline{1}^1_1) - (\overline{1}^1_1\overline{2}^2_2|2^2_2\overline{1}^1_1)\} \ , \ K_{19} = 0.0015848 \ , \ N_{15} = \sqrt{15}$$

$$({}^1S)\Psi_{20} = N_{20}0^t_{oo}(2s^2s1s2) = N_{20}0^t_{oo}(s^2o^1|o^2s^2) = \frac{1}{\sqrt{2}}\{(s^2o^1|o^2s^2) + (s^2o^2|o^1s^2)\} \ , \ K_{20} = 0.0102900 \ , \ N_{20} = \sqrt{2}$$

$$({}^1S)\Psi_{21} = N_{21}0^t_{oo}0^s_{oo}(1s2sp1^2) = N_{21}0^t_{oo}0^s_{oo}(s^1o^1_1|o^1_1s^2) = \frac{1}{6}\{(s^1o^1_1|o^1_1s^2) + (o^1_1s^2|s^1o^1_1) - (s^1\overline{1}^1_1|\overline{1}^1_1s^2) - (s^1\overline{1}^1_1|1^1_1s^2) - (\overline{1}^1_1s^2|s^1\overline{1}^1_1) - (1^1_1s^2|s^1\overline{1}^1_1)\} \ , \ K_{21} = 0.0065906 \ , \ N_{21} = \sqrt{6}$$

TABLE 6 continued

$$({}^1S)\Psi_{22} = N_{22}O^{L}_{oo}(2s^2g2^2) = N_{22}O^{L}_{oo}(s^2o^2_4|o^2_4s^2) = \frac{1}{\sqrt{9}}\{(s^2o^2_4|o^2_4s^2) - (s^2\bar{1}^2_4|1^2_4s^2) - (s^2\bar{1}^2_4|1^2_4s^2) + (s^2\bar{2}^2_4|\bar{2}^2_4s^2) + (s^2\bar{2}^2_4|2^2_4s^2) - (s^2\bar{3}^2_4|\bar{3}^2_4s^2) - (s^2\bar{3}^2_4|3^2_4s^2) + (s^2\bar{4}^2_4|\bar{4}^2_4s^2) + (s^2\bar{4}^2_4|4^2_4s^2)\}$$

$$K_{22} = -0.0008295 \ , \ N_{22} = \sqrt{9}$$

$$({}^1S)\Psi_{23} = N_{23}O^{L}_{oo}O^{S}_{oo}(2s^2p3p4) = N_{23}O^{L}_{oo}O^{S}_{oo}(s^2o^3_1|o^4_1s^2) = \frac{1}{6}\{(s^2o^3_1|o^4_1s^2) + (s^2o^4_1|o^3_1s^2) - (s^2\bar{1}^3_1|\bar{1}^4_1s^2) - (s^2\bar{1}^3_1|1^4_1s^2) - (s^2\bar{1}^4_1|1^3_1s^2) - (s^2\bar{1}^4_1|\bar{1}^3_1s^2)\} \ , \ K_{23} = 0.0000858 \ , \ N_{23} = \sqrt{6}$$

$$({}^1S)\Psi_{24} = N_{24}O^{L}_{oo}(2s^2s3s4) = N_{24}O^{L}_{oo}(s^2o^3|o^4s^2) = \frac{1}{\sqrt{2}}\{(s^2o^3|o^4s^2) + (s^2o^4|o^3s^2)\} \ , \ K_{24} = -0.0057483 \ , \ N_{24} = \sqrt{2}$$

$$({}^1S)\Psi_{25} = N_{25}O^{L}_{oo}(2s^2s1s4) = N_{25}O^{L}_{oo}(s^2o^1|o^4s^2) = \frac{1}{\sqrt{2}}\{(s^2o^1|o^4s^2) + (s^2o^4|o^1s^2)\} \ , \ K_{25} = -0.0049320 \ , \ N_{25} = \sqrt{2}$$

$$({}^1S)\Psi_{26} = N_{26}O^{L}_{oo}O^{S}_{oo}(2s^2p2p4) = N_{26}O^{L}_{oo}O^{S}_{oo}(s^2o^2_1|o^4_1s^2) = \frac{1}{\sqrt{6}}\{(s^2o^2_1|o^4_1s^2) + (s^2o^4_1|o^2_1s^2) - (s^2\bar{1}^2_1|\bar{1}^4_1s^2) - (s^2\bar{1}^2_1|1^4_1s^2) - (s^2\bar{1}^4_1|1^2_1s^2) - (s^2\bar{1}^4_1|\bar{1}^2_1s^2)\} \ , \ K_{26} = -0.0021912 \ , \ N_{26} = \sqrt{6}$$

$$({}^1S)\Psi_{27} = N_{27}O^{L}_{oo}(1s^2p5^2) = NO^{L}_{oo}(s^1o^5_1|o^5_1s^1) = \frac{1}{\sqrt{3}}\{(s^1o^5_1|o^5_1s^1) - (s^1\bar{1}^5_1|\bar{1}^5_1s^1) - (s^1\bar{1}^5_1|1^5_1s^1)\} \ , \ K_{27} = -0.0008337 \ , \ N_{27} = \sqrt{3}$$

TABLE 6 continued

$$(^1S)\Psi_{28} = N_{28}0^4_{00}0^6_{00}(1s^2p1p5) = N_{28}0^4_{00}0^6_{00}(s^1o^1_1|o^5_1s^1) =$$

$$\frac{1}{\sqrt{6}}\{(s^1o^1_1|o^5_1s^1) + (s^1o^5_1|o^1_1s^1) - (s^1\bar{1}^1_1|\bar{1}^5_1s^1) - (s^1\bar{1}^5_1|\bar{1}^1_1s^1) -$$

$$(s^1\bar{1}^5_1|1^1_1s^1) - (s^1\bar{1}^1_1|1^5_1s^1)\} \quad , K_{28} = 0.00013765 \quad , N_{28} = \sqrt{6}$$

$$(^1S)\Psi_{29} = N_{29}0^4_{00}0^6_{00}(2s^2d2d3) = N_{29}0^4_{00}0^6_{00}(s^2o^2_2|o^3_2s^2) =$$

$$\frac{1}{\sqrt{10}}\{(s^2o^2_2|o^3_2s^2) + (s^2o^3_2|o^2_2s^2) - (s^2\bar{1}^2_2|1^3_2s^2) - (s^21^2_2|\bar{1}^3_2s^2) -$$

$$(s^2\bar{1}^3_2|1^2_2s^2) - (s^21^3_2|\bar{1}^2_2s^2) + (s^2\bar{2}^2_2|2^3_2s^2) + (s^22^2_2|\bar{2}^3_2s^2) +$$

$$(s^22^3_2|\bar{2}^2_2s^2) + (s^2\bar{2}^3_2|2^2_2s^2)\} \quad , K_{29} = -0.0015543 \quad , N_{29} = \sqrt{10}$$

$$(^1S)\Psi_{30} = N_{30}0^4_{00}(2s^2f3^2) = N_{30}0^4_{00}(s^2o^3_3|o^3_3s^2) = \frac{1}{\sqrt{7}}\{(s^2o^3_3|o^3_3s^2) -$$

$$(s^21^3_3|\bar{1}^3_3s^2) - (s^2\bar{1}^3_3|1^3_3s^2) + (s^2\bar{2}^3_3|\bar{2}^3_3s^2) + (s^2\bar{2}^3_3|2^3_3s^2) -$$

$$(s^22^3_3|\bar{2}^3_3s^2) - (s^2\bar{2}^3_3|3^3_3s^2)\} \quad , K_{30} = -0.0004808 \quad , N_{30} = \sqrt{7}$$

$$(^1S)\Psi_{31} = N_{31}0^4_{00}(2s^2d4^2) = N_{31}0^4_{00}(s^2o^4_2|o^4_2s^2) = \frac{1}{\sqrt{5}}\{(s^2o^4_2|o^4_2s^2) -$$

$$(s^21^4_2|\bar{1}^4_2s^2) - (s^2\bar{1}^4_2|1^4_2s^2) + (s^2\bar{2}^4_2|\bar{2}^4_2s^2) + (s^2\bar{2}^4_2|2^4_2s^2)\}$$

$$K_{31} = -0.0004351 \quad , N_{31} = \sqrt{5}$$

$$(^1S)\Psi_{32} = AN_{32}0^4_{00}[p2^2][d1^2] = \frac{1}{\sqrt{15}}\{(o^2_1o^1_2|o^1_2o^2_1) - (o^2_11^1_2|\bar{1}^1_2o^2_1) -$$

$$(o^2_1\bar{1}^1_2|1^1_2o^2_1) + (o^2_1\bar{2}^1_2|\bar{2}^1_2o^2_1) + (o^2_1\bar{2}^1_2|2^1_2o^2_1) - (1^2_1o^1_2|o^1_21^2_1) +$$

$$(1^2_11^1_2|\bar{1}^1_21^2_1) + (1^2_1\bar{1}^1_2|1^1_21^2_1) - (1^2_1\bar{2}^1_2|\bar{2}^1_21^2_1) - (1^2_1\bar{2}^1_2|2^1_21^2_1) -$$

$$(\bar{1}^2_1o^1_2|o^1_21^2_1) + (\bar{1}^2_11^1_2|\bar{1}^1_21^2_1) + (\bar{1}^2_1\bar{1}^1_2|1^1_21^2_1) - (\bar{1}^2_1\bar{2}^1_2|\bar{2}^1_21^2_1) -$$

$$(\bar{1}^2_1\bar{2}^1_2|2^1_21^2_1)\} \quad , K_{32} = 0.0004639 \quad , N_{32} = \sqrt{15}$$

TABLE 6 continued

$({}^1S)\Psi_{33} = (2s^2 4s^2) = (s^2 0^4 | 0^4 s^2)$, $K_{33} = 0.0020928$, $N_{33} = 1$

$({}^1S)\Psi_{34} = N_{34} 0^4_{00} (2s^2 3s^2) = N_{34} 0^4_{00} 0^5_{00} (s^2 0^3_4 | 0^3_4 s^2) = \frac{1}{\sqrt{9}} \{ (s^2 0^3_4 | 0^3_4 s^2) -$
$(s^2 1^3_4 | \bar{1}^3_4 s^2) - (s^2 \bar{1}^3_4 | 1^3_4 s^2) + (s^2 2^3_4 | \bar{2}^3_4 s^2) + (s^2 \bar{2}^3_4 | 2^3_4 s^2) -$
$(s^2 3^3_4 | \bar{3}^3_4 s^2) - (s^2 \bar{3}^3_4 | 3^3_4 s^2) + (s^2 4^3_4 | \bar{4}^3_4 s^2) + (s^2 \bar{4}^3_4 | 4^3_4 s^2) \}$

$K_{34} = -0.0002745$, $N_{34} = \sqrt{9}$

$({}^1S)\Psi_{35} = N_{35} 0^4_{00} (2s^2 p1^2) = N_{35} 0^4_{00} (s^2 0^1_1 | 0^1_1 s^2) = \frac{1}{\sqrt{3}} \{ (s^2 0^1_1 | 0^1_1 s^2) -$
$(s^2 1^1_1 | \bar{1}^1_1 s^2) - (s^2 \bar{1}^1_1 | 1^1_1 s^2) \}$, $K_{35} = -0.0018990$, $N_{35} = \sqrt{3}$

$({}^1S)\Psi_{36} = N_{36} 0^4_{00} 0^5_{00} (1s^2 p1p2) = N_{36} 0^4_{00} 0^5_{00} (s^1 0^1_1 | 0^2_1 s^1) =$
$\frac{1}{\sqrt{6}} \{ (s^1 0^1_1 | 0^2_1 s^1) + (s^1 0^2_1 | 0^1_1 s^1) - (s^1 1^1_1 | \bar{1}^2_1 s^1) - (s^1 \bar{1}^1_1 | 1^2_1 s^1) -$
$(s^1 \bar{1}^2_1 | 1^1_1 s^1) - (s^1 1^2_1 | \bar{1}^1_1 s^1) \}$, $K_{36} = 0.0025567$, $N_{36} = 6$

$({}^1S)\Psi_{37} = N_{37} 0^4_{00} 0^5_{00} (1s^2 p2^2) = N_{37} 0^4_{00} 0^5_{00} (s^1 0^2_1 | 0^2_1 s^1) =$
$\frac{1}{\sqrt{3}} \{ (s^1 0^2_1 | 0^2_1 s^1) - (s^1 1^2_1 | \bar{1}^2_1 s^1) - (s^1 \bar{1}^2_1 | 1^2_1 s^1) \}$

$K_{37} = -0.0003084$, $N_{37} = \sqrt{3}$

CHAPTER IV

THE FIRST ORDER DENSITY MATRIX

Symmetry Properties of the First Order Density Matrix

The symmetry properties of the first order density matrix have been investigated by a number of authors (1,30,31). Their investigations have shown that the first order density matrix can be split into two matrices consisting either of all α functions or all β functions. This splitting can be represented as $\begin{pmatrix} A_\alpha & 0 \\ 0 & A_\beta \end{pmatrix}$ where A_α is a submatrix in $\mathcal{H}$ space representing only α functions. The submatrices A_α and A_β are identical, and the submatrices 0 are matrices containing all zero elements.

The splitting of the first order density matrix served as a check on the calculation. Another type of splitting is also present (30). This type of splitting is due to the m_ℓ quantum number in contrast to the other type of splitting due to the m_s quantum number. Each A matrix split into as many identical blocks as the m values could take for various ℓ values. Each block is restricted to functions all of the same ℓ value. The first order density matrix is tabulated in Table 7. Since the matrix is symmetric, we have given only the upper triangular portion, the $i\,j$ element being indicated by $\gamma(\psi_i|\psi_j)$. The notation can readily be translated into basis orbitals by referring to Table 1. The m_ℓ values are

indicated for example, $\psi_7(r),0$ where 0 is the m_ℓ value. Thus the function is $p1,0$.

The Accuracy of the Calculation

Four methods of checking the accuracy of the results were employed. These were as follows:

The trace of the first order density matrix, $\sum_{k=1}^{N} D'(k)$, should be equal to the number of electrons in the system. In the case of the Be atom, it is four, so that the trace of the matrix calculated here should be four to at least seven decimal places. The trace of the undiagonalized matrix including all of the 146 diagonal elements is 4.00000005. The trace of the diagonalized matrix is 4.00000004.

It should be emphasized that although the trace checks to the required accuracy, the off-diagonal elements are not necessarily correct. A partial check on the off-diagonal elements is provided by the fact that the first order density matrix is positive-semidefinite. Thus all the eigenvalues should be positive or zero. Even small errors in the off-diagonal elements can give rise to negative eigenvalues.

The writer found it necessary to check the larger blocks four times until all the eigenvalues became positive. Since the program used to diagonalize the first order density matrix gave the eigenvalues in floating point notation, an extremely small negative eigenvalue could be detected. For example, -12×10^{-20} was not accepted.

A third check on the accuracy of the calculation is the requirement that the density matrices be Hermitian, or symmetric in the special case of real elements. We found that the first order density matrix

calculated from Watson's wave function was real and symmetric.

Since the density matrix was symmetric, it could be diagonalized by an orthogonal transformation. The program which diagonalized the matrix accepted only symmetric matrices so that the fact that it produced an orthogonal transformation was not a real check on the accuracy of the calculation. The only case where checking the orthogonality of the matrix which diagonalized the density matrix was of value was in the hand diagonalization of the two by two matrices. It was a check in this case because it insured the writer he had not made an error in finding the orthogonal transformation.

For the purposes of later reference, these checks will be called respectively, the trace check, the negative eigenvalue check, the symmetry check, and the orthogonality check.

The Results

The results of the diagonalization of the matrix are tabulated in Table 8. It is interesting to note that each block consists of linear combinations of functions of only one type. The reason for this is not difficult to see, for Watson's wave function contains only configurations of the type $\mu\nu\omega\chi$ where μ and ν have the same ℓ, and ω and χ have the same ℓ. The occupation numbers are designated as N'_{ℓ}.

The traditional Hartree-Fock approximation to the Be atom assigns the four electrons to the various shells so that the ground state of the Be atom is designated $1s^2 2s^2$. We see from Table 8 that the first natural 1-state is mostly $1s$ and has an occupancy number of 0.99893058. Also the second natural 1-state is mostly $2s$ with

an occupancy number of 0.9985738. Thus, we may replace (32) the Hartree-Fock ground designation $1s^2\,2s^2$ by $(1s')^{1.9966}\,(2s')^{1.8372}\,(2p')^{0.1622}\,(3d')^{0.0014}$ ... where

$$1s' = -.99989824(1s) + .01425921\,(2s) \qquad (4.1)$$

$$2s' = .01425921(1s) + .99989824(2s) \qquad (4.2)$$

and so forth. This shows that more of the correlation energy (the energy difference between the energy calculated by the Hartree-Fock method and the exact energy, $E_{exact} - E_{HF}$ is due to correlation in the $2s$ shell than in the $1s$ shell. Watson found that about half the correlation energy was due to the $1s^2\,2p^2$ configuration and slightly less than half due to correlation in the $1s$ shell. Since we were more interested in the expansions, we made no energy calculations. Thus we did not find the exact correlations of the various states.

Watson points out in the conclusion of his paper that a better choice of the basis functions would contribute to a better Be energy with as many configurations as he used. We see that he could have improved his basis functions by taking linear combinations of basis functions as shown in Table 8. It would be interesting to find the energy using the natural 1-states as basis functions in Watson's original configurations.

The natural 3-states are found by integrating the product of each natural 1-state with the wave function

$$\Psi_k(2,3,4) = (4/N'_k)^{1/2} \int \Sigma_i K_i \Psi_i \, g^*_k(1)\, dx_1 \qquad (4.3)$$

Since we found 146 natural states, there are 146 terms in the one-three expansion (4.3). Watson's wave function consisted of 203 Slater determinants. Of course, a one-three expansion could have been made in the original basis (also giving 146 terms), but the convergence would be slower. We found by inspection that the first $\mathcal{G}_k(2,3,4)$ contained over 160 3 x 3 determinants, and the others were of similar complexity. We concluded that since the two-two expansion was simpler to interpret and obtain, it was not necessary to calculate the $\mathcal{G}_k$'s .

Shull and Löwdin (33,40) have shown that the natural 1-states are important in interpreting the Coulomb correlation for He , and they (34) made a detailed study of two-electron systems in general. The study by Hirschfelder and Löwdin (35) of the long range interaction of two 1s -hydrogen atoms is also of importance in showing how the natural 1-states simplify the wave function. Shull (17) later (1959) stated that the second order density matrix would be of fundamental importance in solving problems connected with more complex systems, where the geminals would become "the wave-mechanical correspondence of the chemists' 'bond'." He indicated that one should make a natural 1-state analysis of the natural 2-states.

Later publications by Shull (36) and Allen and Shull (37) stressed the importance of the geminals, but still no natural geminals had been calculated.

The first order density matrix served as a check on the second order density matrix. By calculating a few terms of the first order density matrix, from the second order density matrix, we were able to partially verify the internal consistency of the calculations.

TABLE 7

FIRST ORDER DENSITY MATRIX*

i	j		$\psi_i \cdot \psi_j$**	$\gamma(\psi_i \mid \psi_j)$
1	1	0	$\psi_1 \cdot \psi_1$	.9982896
1	2	0	$\psi_1 \cdot \psi_2$	-.001136803
2	2	0	$\psi_2 \cdot \psi_2$	.9185900
3	3	0	$\psi_3 \cdot \psi_3$	.000668306
3	4	0	$\psi_3 \cdot \psi_4$	-.000169239
3	5	0	$\psi_3 \cdot \psi_5$	.000014175
3	6	0	$\psi_3 \cdot \psi_6$	.000073818
4	4	0	$\psi_4 \cdot \psi_4$	.000052942
4	5	0	$\psi_4 \cdot \psi_5$	.000000000...
4	6	0	$\psi_4 \cdot \psi_6$	-.000025375
5	5	0	$\psi_5 \cdot \psi_6$	.000016625
5	6	0	$\psi_5 \cdot \psi_6$	-.000009810
6	6	0	$\psi_6 \cdot \psi_6$	.000033064
7	7	1	$\psi_7 \cdot \psi_7$	.02703291
7	8	1	$\psi_7 \cdot \psi_8$	-.00012509
7	9	1	$\psi_7 \cdot \psi_9$	.0000063898
7	10	1	$\psi_7 \cdot \psi_{10}$	.0000026931
7	11	1	$\psi_7 \cdot \psi_{11}$	-.000092561
8	8	1	$\psi_8 \cdot \psi_8$	.000275106
8	9	1	$\psi_8 \cdot \psi_9$	.000038392
8	10	1	$\psi_8 \cdot \psi_{10}$	.000013964
8	11	1	$\psi_8 \cdot \psi_{11}$	.00000058655
9	9	1	$\psi_9 \cdot \psi_9$	.000013326
9	10	1	$\psi_9 \cdot \psi_{10}$	.0000017751
9	11	1	$\psi_9 \cdot \psi_{11}$	.0000000000...
10	10	1	$\psi_{10} \cdot \psi_{10}$	.0000011153
10	11	1	$\psi_{10} \cdot \psi_{11}$	.0000000000...
11	11	1	$\psi_{11} \cdot \psi_{11}$	.00000053475

TABLE 7 continued

i	j		$\psi_i \cdot \psi_j$ **	$\gamma(\psi_i \mid \psi_j)$
12	12	2	$\psi_{12} \cdot \psi_{12}$	.0000066462
13	13	2	$\psi_{13} \cdot \psi_{13}$	.0000077067
13	14	2	$\psi_{13} \cdot \psi_{14}$	.0000017301
14	14	2	$\psi_{14} \cdot \psi_{14}$	.0000010182
15	15	2	$\psi_{15} \cdot \psi_{15}$	.00000003786
16	16	3	$\psi_{16} \cdot \psi_{16}$	.00000048119
17	17	3	$\psi_{17} \cdot \psi_{17}$	.00000003303
18	18	4	$\psi_{18} \cdot \psi_{18}$	.00000007646
19	19	4	$\psi_{19} \cdot \psi_{19}$	.000000008372

* $\gamma(x_1 \mid x_1') = \sum_{ij} \psi_i \cdot \psi_j [\alpha(\zeta_1)\alpha(\zeta_1') + \beta(\zeta_1)\beta(\zeta_1')] \cdot \gamma(\psi_i \mid \psi_j)$

** $\psi_i \cdot \psi_j = [(\psi_i(r_1),-\ell)(\psi_j^*(r_1'),-\ell) + \cdots + (\psi_i(r_1),-1)(\psi_i^*(r_1'),-1)$

$+ (\psi_i(r_1),0)(\psi_j^*(r_1'),0) + (\psi_i(r_1),1)(\psi_j^*(r_1'),1) + \cdots$

$+ (\psi_i(r_1),\ell)(\psi_j^*(r_1'),\ell)]$

TABLE 8

EIGENVALUES AND EIGENVECTORS OF FIRST ORDER DENSITY MATRIX*

$N_k^1(2)$	.998306					
k	1	2				
Coefficients	Basis Functions					
-.999898	1s	$\overline{1s}$				
.014259	2s	$\overline{2s}$				
$N_k^1(2)$	.918574					
k	3	4				
Coefficients	Basis Functions					
.014259.	1s	$\overline{1s}$				
.999898	2s	$\overline{2s}$				
$N_k^1(6)$	.027034					
k	5	6	7	8	9	10
Coefficients	Basis Functions					
.999983	p1,0	$\overline{p1,0}$	p1,1	$\overline{p1,1}$	p1,-1	$\overline{p1,-1}$
-.004674	p2,0	$\overline{p2,0}$	p2,1	$\overline{p2,1}$	p2,-1	$\overline{p2,-1}$
.000230	p3,0	$\overline{p3,0}$	p3,1	$\overline{p3,1}$	p3,-1	$\overline{p3,-1}$
.000097	p4,0	$\overline{p4,0}$	p4,1	$\overline{p4,1}$	p3,-1	$\overline{p3,-1}$
-.003424	p5,0	$\overline{p5,0}$	p5,1	$\overline{p5,1}$	p5,-1	$\overline{p5,-1}$

TABLE 8 continued

$N_k^1(2)$	.00072081					
k	11	12				
Coefficients	Basis Functions					
.962067	s1	$\overline{s1}$				
-.248051	s2	$\overline{s2}$				
.017804	s3	$\overline{s3}$				
.112160	s4	$\overline{s4}$				
$N_k^1(6)$	.00028077					
k	13	14	15	16	17	18
Coefficients	Basis Functions					
.004585	p1,0	$\overline{p1,0}$	p1,1	$\overline{p1,1}$	p1,-1	$\overline{p1,-1}$
.988526	p2,0	$\overline{p2,0}$	p2,1	$\overline{p2,1}$	p2,-1	$\overline{p2,-1}$
.142350	p3,0	$\overline{p3,0}$	p3,1	$\overline{p3,1}$	p3,-1	$\overline{p3,-1}$
.050309	p4,0	$\overline{p4,0}$	p4,1	$\overline{p4,1}$	p4,-1	$\overline{p4,-1}$
.000555	p5,0	$\overline{p5,0}$	p5,1	$\overline{p5,1}$	p5,-1	$\overline{p5,-1}$
$N_k^1(10)$	.00006462					
k	19	20	21	22	23	24
Coefficients	Basis Functions					
1	d1,0	$\overline{d1,0}$	d1,1	$\overline{d1,1}$	d1,-1	$\overline{d1,-1}$
k continued	25	26	27	28		
	d1,2	$\overline{d1,2}$	d1,-2	$\overline{d1,-2}$		

TABLE 8 continued

$N_k^1(2)$	.000034304					
k	29	30				
Coefficients	Basis Functions					
-.144667	s1	$\overline{s1}$				
-.246107	s2	$\overline{s2}$				
-.551090	s3	$\overline{s3}$				
.784093	s4	$\overline{s4}$				
$N_k^1(2)$	.0000087224					
k	31	32				
Coefficients	Basis Functions					
.168441	s1	$\overline{s1}$				
.414781	s2	$\overline{s2}$				
-.799436	s3	$\overline{s3}$				
-.400607	s4	$\overline{s4}$				
$N_k^1(10)$	.0000081277					
k	33	34	35	36	37	38
Coefficients	Basis Functions					
.97164	d2,0	$\overline{d2,0}$	d2,1	$\overline{d2,1}$	d2,-1	$\overline{d2,-1}$
.23645	d3,0	$\overline{d3,0}$	d3,1	$\overline{d3,1}$	d3,-1	$\overline{d3,-1}$
k continued	39	40	41	42		
	d2,2	$\overline{d2,2}$	d2,-2	$\overline{d2,-2}$		
	d3,2	$\overline{d3,2}$	d3,-2	$\overline{d3,-2}$		

TABLE 8 continued

$N_k^1(6)$	.0000077971					
k	43	44	45	46	47	48
Coefficients	Basis Functions					
-.000883	p1,0	$\overline{p1,0}$	p1,1	$\overline{p1,1}$	p1,-1	$\overline{p1,-1}$
-.140868	p2,0	$\overline{p2,0}$	p2,1	$\overline{p2,1}$	p2,-1	$\overline{p2,-1}$
.989516	p3,0	$\overline{p3,0}$	p3,1	$\overline{p3,1}$	p3,-1	$\overline{p3,-1}$
-.031843	p4,0	$\overline{p4,0}$	p4,1	$\overline{p4,1}$	p4,-1	$\overline{p4,-1}$
-.000117	p5,0	$\overline{p5,0}$	p5,1	$\overline{p5,1}$	p5,-1	$\overline{p5,-1}$

$N_k^1(2)$	.0000071016	
k	49	50
Coefficients	Basis Functions	
.158509	s1	$\overline{s1}$
.840154	s2	$\overline{s2}$
.238504	s3	$\overline{s3}$
.460578	s4	$\overline{s4}$

$N_k^1(10)$	.00000059714					
k	51	52	53	54	55	56
Coefficients	Basis Functions					
.23645	d2,0	d2,0	d2,1	d2,1	d2,-1	d2,-1
-.97164	d3,0	d3,0	d3,1	d3,1	d3,-1	d3,-1
k continued	57	58	59	60		
	d2,2	d2,2	d2,-2	d2,-2		
	d3,2	d3,2	d3,-2	d3,-2		

TABLE 8 continued

$N_k^1(14)$	.000000048119					
k	61	62	63	64	65	66
Coefficients	Basis Functions					
1	f2,0	$\overline{f2,0}$	f2,1	$\overline{f2,1}$	f2,-1	$\overline{f2,-1}$
k continued	67	68	69	70	71	72
	f2,2	$\overline{f2,2}$	f2,-2	$\overline{f2,-2}$	f2,3	$\overline{f2,3}$
k continued	73	74				
	f2,-3	$\overline{f2,-3}$				
$N_k^1(6)$	.00000039790					
k	75	76	77	78	79	80
Coefficients	Basis Functions					
-.003424	p1,0	$\overline{p1,0}$	p1,1	$\overline{p1,1}$	p1,-1	$\overline{p1,-1}$
.000555	p2,0	$\overline{p2,0}$	p2,1	$\overline{p2,1}$	p2,-1	$\overline{p2,-1}$
.000117	p3,0	$\overline{p3,0}$	p3,1	$\overline{p3,1}$	p3,-1	$\overline{p3,-1}$
.006835	p4,0	$\overline{p4,0}$	p4,1	$\overline{p4,1}$	p4,-1	$\overline{p4,-1}$
.999970	p5,0	$\overline{p5,0}$	p5,1	$\overline{p5,1}$	p5,-1	$\overline{p5,-1}$
$N_k^1(6)$	.000000023047					
k	81	82	83	84	85	86
Coefficients	Basis Functions					
-.000333	p1,0	$\overline{p1,0}$	p1,1	$\overline{p1,1}$	p1,-1	$\overline{p1,-1}$
-.054319	p2,0	$\overline{p2,0}$	p2,1	$\overline{p2,1}$	p2,-1	$\overline{p2,-1}$
.024416	p3,0	$\overline{p3,0}$	p3,1	$\overline{p3,1}$	p3,-1	$\overline{p3,-1}$
.998201	p4,0	$\overline{p4,0}$	p4,1	$\overline{p4,1}$	p4,-1	$\overline{p4,-1}$
.006855	p5,0	$\overline{p5,0}$	p5,1	$\overline{p5,1}$	p5,-1	$\overline{p5,-1}$

TABLE 8 continued

$N_k^1(18)$	.00000007646					
k	87	88	89	90	91	92
Coefficients	Basis Functions					
1	$g1,0$	$\overline{g1,0}$	$g1,1$	$\overline{g1,1}$	$g1,-1$	$\overline{g1,-1}$
k continued	93	94	95	96	97	98
	$g1,2$	$\overline{g1,2}$	$g1,-2$	$\overline{g1,-2}$	$g1,3$	$\overline{g1,3}$
k continued	99	100	101	102	103	104
	$g1,-3$	$\overline{g1,-3}$	$g1,4$	$\overline{g1,4}$	$g1,-4$	$\overline{g1,-4}$
$N_k^1(10)$	.00000003786					
k	105	106	107	108	109	110
Coefficients	Basis Functions					
	$d4,0$	$\overline{d4,0}$	$d4,1$	$\overline{d4,1}$	$d4,-1$	$\overline{d4,-1}$
k continued	111	112	113	114		
	$d4,2$	$\overline{d4,2}$	$d4,-2$	$\overline{d4,-2}$		
$N_k^1(14)$	.00000003303					
k	115	116	117	118	119	120
Coefficients	Basis Functions					
1	$f3,0$	$\overline{f3,0}$	$f3,1$	$\overline{f3,1}$	$f3,-1$	$\overline{f3,-1}$
k continued	121	122	123	124	125	126
	$f3,2$	$\overline{f3,2}$	$f3,-2$	$\overline{f3,-2}$	$f3,3$	$\overline{f3,3}$
k continued	127	128				
	$f3,-3$	$\overline{f3,-3}$				

TABLE 8 continued

$N_k^1(18)$	.000000008372					
k	129	130	131	132	133	134
Coefficients	Basis Functions					
1	g2,0	$\overline{g2,0}$	g2,1	$\overline{g2,1}$	g2,-1	$\overline{g2,-1}$
k continued	135	136	137	138	139	140
	g2,2	$\overline{g2,2}$	g2,-2	$\overline{g2,-2}$	g2,3	$\overline{g2,3}$
k continued	141	142	143	144	145	146
	g2,-3	$\overline{g2,-3}$	g2,4	$\overline{g2,4}$	g2,-4	$\overline{g2,-4}$

* The eigenvalues are listed as $N_k^1(d)$, where k is the order number with respect to magnitude and d is the degeneracy. We have ordered the eigenvalues so that $N_k^1(d) \geq N_{k+1}^1(d)$. The eigenvectors of a degenerate set are given as a vertical list of coefficients under the eigenvalue with the list of basis functions beside its corresponding coefficient. The vertical list is topped by its k number, and each eigenvector can be found by multiplying the basis function by its corresponding coefficient and algebraically adding. Functions with beta spin are barred, and the M_L value is given after the comma when $\ell > 0$.

CHAPTER V

THE SECOND ORDER DENSITY MATRIX

This chapter contains a discussion of the calculations of the second order density matrix, tables of the eigenvalues and eigenvectors of the second order density matrix and the expansion of the wave function in geminals.

The Calculation

The second order density matrix was calculated from Watson's wave function for the Be atom, by the use of the IBM 709. We used equation (2.11) for this calculation. In practice k was kept less than l and the k's and l's interchanged so that only the upper triangular portion of the matrix was calculated.

The machine program that calculated the matrix is a general program which will accept configuration interaction wave functions, constructed from an orthonormal basis set, for systems with as many as twenty fermions. It uses auxiliary tapes for storage and calculates a master tape in the event that the machine breaks down during a run. The master tape enables the program to be restarted without any loss of intermediate data. The program, as originally written did not contain any provision for restart, but during a run the machine broke down, and we lost all the partial results. The run was calculated to last approximately five hours, but the inclusion of the restart

program increased the run time to approximately twelve hours. We note that the run time for a wave function containing five Slater determinants is only a few seconds. The program is discussed in Appendix II.

In order to make the program as simple as possible the 146 basis functions were coded as integers. The output from the program was punched on cards and also printed. The printed output, which consisted of 6,584 terms, was examined for diagonal elements so that the matrix could be rearranged in smaller blocks. We found 594 diagonal elements which gave one 124 x 124 block, three 14 x 14 blocks, five identical 7 x 7 blocks, one 7 x 7 block which differs slightly from the previous 7 x 7 blocks, four identical 5 x 5 blocks, two identical 4 x 4 blocks, seventeen identical 2 x 2 blocks, and, finally, 322 diagonal elements. The most important blocks of the second order density matrix are exhibited in Appendix I.

The punched card output was rearranged according to the scheme described above, and the cards were used as data for a small format changing program. The format changing program incorporated a routine which multiplied the numbers by a factor in order to retain as many significant figures as possible. The punched card output from the format changing program was used as input to the matrix diagonalization program which was written by Jan Nordling.

This program is designed for matrices no larger than 50 x 50 , so the larger block of order 124 had to be truncated to order 50 . In order to justify the truncation, a theorem was developed by Nordling during a discussion with the writer to estimate the error in the eigenvalues.

Theorem 5.1 If E_i is the ith eigenvalue of a positive-semidefinite matrix

$$\mathbb{H} = \left[\begin{array}{c|c} \mathbb{H}_{mm} & H_{1,m+1} \cdots H_{1,N} \\ \hline H_{m+1,1} & \\ \vdots & \\ H_{N,1} & H_{N,m+1} \cdots H_{N,N} \end{array}\right]$$

of order N, and E_i' is the eigenvalue of the truncated matrix $\mathbb{H}_{mm}$ of order m, then

$$\sum_{i=1}^{m} (E_i - E_i') \leqslant \sum_{i=m+1}^{N} H_{ii} . \qquad (5.1)$$

Proof: From the separation theorem we may write $E_i \geqslant E_i'$, where we have ordered the eigenvalues so that $E_i \geqslant E_{i+1}$ and $E_i' \geqslant E_{i+1}'$. Since the trace is invarient, we may write

$$\sum_{i=1}^{m} E_i \leqslant \sum_{i=1}^{N} H_{ii} , \quad \sum_{i=1}^{m} E_i' = \sum_{i=1}^{m} H_{ii} .$$

Subtracting the equation from the inequality we find

$$\sum_{i=1}^{m} (E_i - E_i') \leqslant \sum_{i=m+1}^{N} H_{ii} . \qquad \text{Q.E.D.}$$

Using (5.1) to estimate the error in the eigenvalue of the truncated matrix, we find

$$\sum_{i=1}^{50} (E_i - E_i') \leqslant 1.6893 \times 10^{-5} .$$

The trace of the 50 x 50 block before diagonalization is 3.8339492; whereas, the trace after diagonalization is 3.8339436. The difference between these two numbers $.56 \times 10^{-5}$ indicates that the round-off errors due to the diagonalization affect the trace only in the seventh significant figure. As expected, the traces of the other

blocks check to at least seven significant figures. The trace of the second order density matrix in the original basis is 5.9999896. This number compares favorably with the actual trace of 6.000000, and shows that the round-off error due to the program for calculating the second order density matrix is negligible.

The Results

Table 9 exhibits the first 50 ordered diagonal elements of the second order density matrix with each element labeled by the product of determinants that it is associated with and the block that it comes from. The notation of the determinants is best explained by an example. For instance, the symbol $1\mathcal{A}\overline{1\mathcal{A}}$ represents the 2 x 2 determinant $|1\mathcal{A}(1)\alpha(1)\ 1\mathcal{A}(2)\beta(2)|$. If we represent the 2 x 2 determinants by $X_i = X_i(1,2)$ and the elements of the second order density matrix by a_{ij}, the expansion of D^2 in coordinate space is written $D^2 = \sum a_{ij} X_i X_j^{*\prime}$ where $X_j^{*\prime} = X_j^*(1',2')$. Diagonalizing D^2 results in $D^2 = \sum_k N_k^2 g_k g_k^{*\prime}$ where g_k is a linear combination of the X_i. For example, the term in the expansion of D^2 in the original basis is

$.99823|1\mathcal{A}(1)\alpha(1)\ 1\mathcal{A}(2)\beta(2)| \times |1\mathcal{A}^*(1')\alpha^*(1')\ 1\mathcal{A}^*(2')\beta^*(2')|$

where .99823 is the first diagonal element.

Functions other than $1\mathcal{A}$, $2\mathcal{A}$, are labeled with the integer after the function and a comma separating the m_ℓ value if $\ell > 0$. For example, the four other $\mathcal{A}$ type functions are labeled $\mathcal{A}1$, $\mathcal{A}2$, $\mathcal{A}3$, $\mathcal{A}4$; whereas for $\ell > 0$ a typical $\mathcal{P}$ type function $\mathcal{P}x$ is labeled $\mathcal{P}1, m_\ell = \begin{cases} \mathcal{P}1,1 \\ \mathcal{P}1,0 \\ \mathcal{P}1,-1 \end{cases}$. A typical determinant

consisting of p and d functions is labeled $p^{1}_{1},-1\,d_{2},1$. We note that since in several cases there are a number of identical blocks, the blocks are labeled with a number in parentheses after the order number of the block to indicate from which particular block that diagonal element came.

It is not strictly accurate to associate the eigenvalues of the second order density matrix with any one particular determinant because the eigenvectors or geminals consist of a linear combination of 2 x 2 determinants. We may say, however, that a particular linear combination is mostly one kind of determinant if that determinant has the largest coefficient in the linear combination. We note that the Schmidt phase convention requires that we integrate the product of each geminal with the wave function to find the associated function $\mathcal{G}_i(3,4)$ in $\Psi = 6^{-1/2} \sum (N^2_k)^{1/2} g_k(1,2)\,\mathcal{G}_k(3,4)$. In the particular case of Watson's wave function equation (2.14) becomes

$$\mathcal{G}_j(3,4) = (6/N^2_j)^{1/2} \int \sum_i K_i\, \psi_i\, g_j^{*}(1,2)\, dx_1\, dx_2 \qquad (5.2)$$

where N^2_j is the j^{th} eigenvalue of the second order density matrix. Table 10 exhibits the eigenvalues labeled with the principal determinants in the eigenfunction. In some cases the eigenvectors $g_k(1,2)$ contain two large coefficients, and are therefore labeled as the sum or difference of two determinants. Table 11 makes this clear by exhibiting the eigenvalue with its corresponding eigenfunction or geminal. A geminal can be identified by its k value, for example, the geminal $g_{10}(1,2)$ is given under the $k = 10$ column.

The eigenvalues of the 50 x 50 block should be rounded off to five figures beyond the decimal. Five figures are probably all we can expect in the diagonalization of a 50 x 50 matrix, as this represents the accuracy of the automatic eigenvalue check in the program. The other eigenvalues are accurate to at least six figures beyond the decimal.

Now we have the eigenvalues and eigenvectors, what information can we glean from them? The first six eigenvalues correspond to the six eigenvalues obtainable from the single Slater determinant in the Hartree-Fock approximation. The eigenvalues in the Hartree-Fock case are all one, and those obtained from Watson's wave function are less than one. If we write these eigenvalues down in decreasing order they are

k	N_k^2	Principal Components of g_k
1	1.000847	$1s\overline{1s} + 2s\overline{2s}$
2	.998926	$1s\overline{1s} - 2s\overline{2s}$
3	.917098	$1s\overline{2s} + 2s\overline{1s}$
4	.916969	$2s\overline{1s} - 1s\overline{2s}$
5	.916971	$\overline{1s2s}$
6	.916971	1s2s

Not all figures are significant; rounding where required gives 1.00085, .99893, .91710, 91697, .916971, .916971.

The last two come from two identical 4 x 4 blocks so their eigenvalues are identical, and their eigenvectors have identical form, so we can be sure that they are accurate to six significant figures.

We may illustrate the calculation of the "pairing" function $\mathcal{Y}_i$ which pairs with g_i as follows: The basis determinants for g_5 and g_6 are

Basis Determinants

First 4 x 4 Block	Second 4 x 4 Block	Eigenvector Coefficients
$1s\overline{2s}$ = $\overline{y1}$	1s2s = y1	.999998 = c1
$\overline{p1},0\overline{p2},0$ = $\overline{y2}$	p1,0p2,0 = y2	-.001082 = c2
$\overline{p1},1\overline{p2},-1$ = $\overline{y3}$	p1,1p2,-1 = y3	.001082 = c3
$\overline{p2},1\overline{p1},-1$ = y4	p2,1p1,-1 = y4	-.001082 = c4

The numbers are the coefficients of the basis determinants. For the sake of convenience, we will refer to the basis determinants as $y1$, $y2$, $y3$, $y4$ respectively and the eigenvector coefficients as $c1$, $c2$, $c3$, and $c4$ respectively.

Inspecting Table 2, we see that the only Φ_i's which will give non-vanishing integrals with these basis determinants are Φ_1, Φ_6, and Φ_{14}. Inspecting the projected Ψ_1, Ψ_6 and Ψ_{14} in Table 6, we see from equation (5.2) that $\mathcal{Y}_5 = -g_6$.

$$\mathcal{Y}_j(3,4) = (6/N_j^2)^{1/2} \int \sum_i K_i \Psi_i g_j^*(1,2)\, dx_1\, dx_2 \qquad (5.2)$$

Thus

$$\mathcal{Y}_5 = (N_5^2)^{-1/2} \{ -(K_1 \times c1)\, y1 + (K_{14}' \times c1)\, y2 + (K_{14}' \times c3)\, y4 - (K_{14}' \times c1)\, y3 \}$$

where $N_5^2 = .916971$; $K_1 = .9575824$; and $K_{14}' = .001034$. The integration with Ψ_6 produces negligible terms.

The other geminal is exactly the same except that the basis determinants contain beta spin functions. This phenomenon is typical when the degenerate eigenfunctions come from different blocks which differ only in the spin functions. Degenerate eigenfunctions in the same block are most easily discussed using symmetry considerations (see Chapter VI).

The first 54 $\mathcal{A}_k$'s in the geminal expansion are in Table 12. The simplicity of this two-two expansion is particularly striking. We were able to obtain this expansion simply by inspecting the first few terms for the phase factor $+|$ or $-|$, and using the Carlson-Keller (16) theorem.

One might think that the eigenvalue 1.00085 would be 1.00000 but for round-off error, but careful checks indicate that this eigenvalue is probably correct. The theory of density matrices also allows this eigenvalue to go as high as two.

Accuracy of the Calculation

The trace check, negative eigenvalue check, and symmetry check were supplemented in the case of the geminals by two other checks. These were as follows:

1. One must be able to reconstruct the wave function from the natural expansion (equation 5.2). In particular we should be able to pick out the three coefficients $K_1 = .9576$, $K_2 = -.2845$, and $K_4 = -.02326$ of configurations 1, 2, and 4 respectively, and terms like $|1\bar{\Delta}(1)\,1\bar{\Delta}(2)| \times |1\bar{\Delta}(3)\,1\bar{\Delta}(4)|$ should vanish, for they are not in the wave function. Such terms were checked and found to have small positive or negative coefficients of the order of .001

after only four terms in (5.2) were included in the calculation. The writer feels that since there are over one hundred geminals to be summed, it seems reasonable that they are truly vanishing. This will be thoroughly checked later. The other terms mentioned were checked and found to agree to three figures when only four geminals were included in the calculation. All evidence from this check indicates that the geminals are correct.

2. We must be able to calculate the first order density matrix from the second order density matrix. A few diagonal elements of the first order density matrix were chosen, and we calculated these diagonal elements to three figure accuracy from the second order density matrix. A spot check was also made of an off-diagonal element of the first order density matrix calculated from the second order density matrix. The results showed that the second order density matrix was consistent with the first order density matrix.

TABLE 9

THE FIRST 50 DIAGONAL ELEMENTS OF THE SECOND ORDER DENSITY MATRIX IN THE ORIGINAL BASIS*

Determinant	Diagonal Element	Blocks	Symmetry	M_S	M_L
$1s\overline{1s}$	.998223	124	I	0	0
$2s\overline{2s}$	.918523	124	I	0	0
$1s\overline{2s}$	.917029	124	I + III	0	0
$2s\overline{1s}$	.917029	124	I + III	0	0
$\overline{1s}2s$	.916968	4(1)	III	-1	0
1s2s	.916968	4(2)	III	1	0
$p1,0\overline{p1},0$	.027016	124	I	0	0
$p1,1\overline{p1},-1$	.027016	124	I + III	0	0
$p1,-1\overline{p1},1$	.027016	124	I + III	0	0
1sp1,0	.026985	7(1)	III	1	0
$\overline{1sp1},0$	.026985	7(2)	III	-1	0
1sp1,-1	.026985	7(6)	III	1	-1
$\overline{1sp1},1$	.026985	7(3)	III	-1	1
$\overline{1sp1},-1$	.026985	7(4)	III	-1	-1
1sp1,1	.026985	7(5)	III	1	1
$1s\overline{p1},-1$	.026983	14(1)	I + III	0	-1
$\overline{1s}p1,1$	.026983	14(3)	I + III	0	1
$\overline{1s}p1,-1$	.026983	14(1)	I + III	0	-1
$1s\overline{p1},1$	.026983	14(3)	I + III	0	1
$1s\overline{p1},0$	.026983	14(2)	I + III	0	0
$p1,0\overline{1s}$	.026983	14(2)	I + III	0	0
$s1\overline{2s}$	.0006212	5(1)	I + III	0	0
$2ss\overline{1}$	.0006212	5(2)	I + III	0	0
$\overline{2ss1}$	.0006212	5(3)	III	-1	0
2ss1	.0006212	5(4)	III	1	0
$p2,0\overline{p2},0$	.0002532	124	I	0	0
$p2,1\overline{p2},-1$	.0002532	124	I + III	0	0
$p2,-1\overline{p2},1$	.0002532	124	I + III	0	0
2sp2,0	.0002514	7(1)	III	1	0

TABLE 9 continued

Determinant	Diagonal Element	Blocks	Symmetry	M_S	M_L
$\overline{2sp2},0$	.0002514	7(2)	III	-1	0
$\overline{2sp2},1$	.0002514	7(3)	III	-1	1
$\overline{2sp2},\overline{-1}$	.0002514	7(4)	III	-1	-1
2sp2,1	.0002514	7(5)	III	1	1
2sp2,-1	.0002514	7(6)	III	1	-1
$2\overline{sp2},\overline{-1}$	.0002493	14(1)	I + III	0	-1
$\overline{2sp2},-1$	.0002493	14(1)	I + III	0	-1
$2\overline{sp2},0$	.0002493	14(2)	I + III	0	0
$p2,0\overline{2s}$	.0002493	14(2)	I + III	0	0
$2\overline{sp2},1$	.0002493	14(3)	I + III	0	1
$\overline{2sp2},1$	.0002493	14(3)	I + III	0	1
$d1,0\overline{d1},0$	.0000665	124	I	0	0
$d1,1\overline{d1},\overline{-1}$	.0000665	124	I + III	0	0
$d1,-1\overline{d1},1$	.0000665	124	I + III	0	0
$d1,2\overline{d1},\overline{-2}$	.0000665	124	I + III	0	0
$d1,-2\overline{d1},2$	.0000665	124	I + III	0	0
lsd1,0	.0000665	1	III	1	0
lsd1,1	.0000665	1	III	1	1
lsd1,-1	.0000665	1	III	1	-1
lsd2,2	.0000665	1	III	1	2
lsd2,-2	.0000665	1	III	1	-2

Trace = 5.9967884

* The symbol I stands for a singlet, III for a triplet, and I + III for a singlet + triplet. The block number stands for the order of the block, and a number in parenthesis after the order number distinguishes the origin of the diagonal element from identical blocks.

TABLE 10

THE FIRST 54 EIGENVALUES OF THE SECOND ORDER DENSITY MATRIX

Principal Determinants in Eigenvector g_k	Eigenvalue	Block*	S	M_S	M_L	L	k
$1s\overline{1s}$ + $2s\overline{2s}$	1.00085	1^{2}4	0	0	0	0	1
$1s\overline{1s}$ - $2s\overline{2s}$	.99893	1^{2}4	0	0	0	0	2
$1s\overline{2s}$ - $\overline{1s}2s$	.91710	1^{2}4	0	0	0	0	3
$\overline{2s}1s$ + $2s\overline{1s}$	.91700	1^{2}4	1	0	0	0	4
$\overline{1s2s}$	.916971	4(1)	1	-1	0	0	5
1s2s	.916971	4(2)	1	1	0	0	6
1sp1,0	.026999	7(1)	1	1	0	1	7
$\overline{1sp1}$,0	.026999	7(2)	1	-1	0	1	8
$\overline{1sp1}$,-1	.026999	7(3)	1	-1	-1	1	9
1sp1,1	.026999	7(4)	1	1	1	1	10
$\overline{1sp1}$,1	.026999	7(5)	1	-1	1	1	11
1sp1,-1	.026999	7(6)	1	1	-1	1	12
$1s\overline{p1}$,-1 - $\overline{1s}$p1,-1	.026999	14(1)	0	0	-1	1	13
$1s\overline{p1}$,1 + $\overline{1s}$p1,1	.026999	14(2)	1	0	1	1	14
$1s\overline{p1}$,-1 + $\overline{1s}$p1,-1	.026999	14(1)	1	0	-1	1	15
$\overline{1s}$p1,1 - $1s\overline{p1}$,1	.026999	14(2)	0	0	1	1	16
$1s\overline{p1}$,0 - $\overline{1s}$p1,0	.026999	14(3)	0	0	0	1	17
p1,$0\overline{1s}$ - $1s\overline{p1}$,0	.026999	14(3)	1	0	0	1	18
$s1\overline{2s}$ + $2s\overline{s1}$	.000691	5(1)	0	0	0	0	19
$s1\overline{2s}$ - $2s\overline{s1}$	.000691	5(2)	1	0	0	0	20
$\overline{2ss1}$	.000691	5(3)	1	-1	0	0	21
2ss1	.000691	5(4)	1	1	0	0	22
1sp1,0	.000268	7(1)	1	1	0	1	23
$\overline{1sp1}$,0	.000268	7(2)	1	-1	0	1	24
$\overline{1sp1}$,-1	.000255	7(3)	1	-1	-1	1	25
1sp1,1	.000255	7(4)	1	1	1	1	26
$\overline{1sp1}$,1	.000268	7(5)	1	-1	1	1	27
1sp1,-1	.000268	7(6)	1	1	-1	1	28
$2s\overline{p2}$,-1 + $\overline{2s}$p2,-1	.000273	14(1)	1	0	-1	1	29

TABLE 10 continued

Principal Determinants in Eigenvector g_k	Eigenvalue	Block*	S	M_S	M_L	L	k
$\overline{2sp2}$,1 - 2sp$\overline{2}$,1	.000273	14(2)	0	0	1	1	30
2sp$\overline{2}$,-1 - $\overline{2}$sp2, -1	.000268	14(1)	0	0	-1	1	31
2sp$\overline{2}$,1 + $\overline{2sp2}$,1	.000268	14(2)	1	0	1	1	32
p2,0$\overline{2s}$ - 2sp$\overline{2}$,0	.000273	14(3)	1	0	0	1	33
2sp$\overline{2}$,0 + p2,0$\overline{2s}$	.000268	14(3)	0	0	0	1	34
1sd1,0	.000066	D.E.	1	1	0	2	35
1sd1,1	.000066	D.E.	1	1	1	2	36
1sd1,-1	.000066	D.E.	1	1	-1	2	37
1sd1,2	.000066	D.E.	1	1	2	2	38
1sd1,-2	.000066	D.E.	1	1	-2	2	39
(1sd$\overline{1}$,0 + $\overline{1sd1}$,0)/ $\sqrt{2}$	.000066	D.E.	1	0	0	2	40
(1sd$\overline{1}$,1 + $\overline{1sd1}$,1)/ $\sqrt{2}$	.000066	D.E.	1	0	1	2	41
(1sd$\overline{1}$,-1 + $\overline{1sd1}$,-1)/ $\sqrt{2}$	.000066	D.E.	1	0	-1	2	42
(1sd$\overline{1}$,2 + $\overline{1sd1}$,2)/ $\sqrt{2}$	.000066	D.E.	1	0	2	2	43
(1sd$\overline{1}$,-2 + $\overline{1sd1}$,-2)/ $\sqrt{2}$	.000066	D.E.	1	0	-2	2	44
($\overline{1sd1}$,0 - 1sd$\overline{1}$,0)/ $\sqrt{2}$	.000066	D.E.	0	0	0	2	45
($\overline{1sd1}$,1 - 1sd$\overline{1}$,1)/ $\sqrt{2}$	.000066	D.E.	0	0	1	2	46
($\overline{1sd1}$,-1 - 1sd$\overline{1}$,-1)/ $\sqrt{2}$	.000066	D.E.	0	0	-1	2	47
($\overline{1sd1}$,2 - 1sd$\overline{1}$,2)/ $\sqrt{2}$	.000066	D.E.	0	0	2	2	48
($\overline{1sd1}$,-2 - 1sd$\overline{1}$,-2)/ $\sqrt{2}$	.000066	D.E.	0	0	-2	2	49
$\overline{1sd1}$,0	.000066	D.E.	1	-1	0	2	50
$\overline{1sd1}$,1	.000066	D.E.	1	-1	1	2	51
$\overline{1sd1}$,-1	.000066	D.E.	1	-1	-1	2	52
$\overline{1sd1}$,2	.000066	D.E.	1	-1	2	2	53
$\overline{1sd1}$,-2	.000066	D.E.	1	-1	-2	2	54

Trace = 5.999099

* The abbreviation D.E. means diagonal element. We have combined the diagonal elements which consist of mixtures of states into pure singlets and triplets.

TABLE 11

EIGENVALUES AND EIGENVECTORS OF THE SECOND ORDER DENSITY MATRIX

Eigenvalues N_k^2	1.000847	.998926	.917098	.916969
k	1	2	3	4
Basis Determinants		Coefficients		
$1s\overline{1s}$	.704467	.708101	.026730	.000012
$2s\overline{2s}$	.679409	-.675557	-.026449	-.000012
$1s\overline{2s}$	-.000341	-.026034	.706891	-.706794
$2s\overline{1s}$	-.000341	-.026034	.706269	.707416
$p1,\overline{0p1},0$	-.117149	.115266	.000547	.000000
$p1,1\overline{p1},-1$	.117149	-.115266	-.000547	-.000000
$p1,-1\overline{p1},1$	.117148	-.115265	-.000547	-.000000
$s1\overline{s1}$	-.016848	-.017143	.005092	.000002
$p2,0\overline{p2},0$	-.011173	-.011081	.002439	.000001
$p2,1\overline{p2},-1$	.011173	.011081	-.002439	-.000001
$p2,-1\overline{p2},1$	.011173	.011081	-.002439	-.000001
$d1,0\overline{d1},0$	-.005775	.005749	.000227	.000000
$d1,1\overline{d1},-1$	.005775	-.005749	-.000227	-.000000
$d1,-1\overline{d1},1$	.005775	-.005749	-.000227	-.000000
$d1,2\overline{d1},-2$	-.005775	.005749	.000227	.000000
$d1,-2\overline{d1},2$	-.005775	.005749	.000227	.000000
$s1\overline{s2}$	.004915	.004944	.000201	.000000
$s2\overline{s1}$	.004915	.004944	.000201	.000000
$p1,\overline{0p2,0}$	-.001290	-.002869	.002181	.000766
$p2,\overline{0p1,0}$	-.001290	-.002869	.002181	-.000764
$p1,1\overline{p2},-1$	.001290	.002869	-.002181	-.000766
$p2,1\overline{p1},-1$	.001290	.002869	-.002181	.000764
$p1,-1\overline{p2},1$	.001290	.002869	-.002181	-.000766
$p2,-1\overline{p1},1$	.001290	.002869	-.002181	.000764
$s3\overline{s4}$	-.002746	-.002762	-.000112	-.000000
$s4\overline{s3}$	-.002746	-.002762	-.000112	-.000000
$s1\overline{s4}$	-.002356	-.002370	-.000096	-.000000

TABLE 11 continued

Eigenvalues N_k^2	1.000847	.998926	.917089	.916969
k	1	2	3	4
Basis Determinants		Coefficients		
s4s1	-.002356	-.002370	-.000096	-.000000
p3,0$\overline{p3}$,0	-.002006	-.002018	-.000082	-.000000
p3,1$\overline{p3}$,-1	.002006	.002018	.000082	.000000
p3,-1$\overline{p3}$,1	.002006	.002018	.000082	.000000
d2,1$\overline{d2}$,-1	.001925	.001935	.000074	.000000
d2,-1$\overline{d2}$,1	.001925	.001935	.000074	.000000
d2,2$\overline{d2}$,-2	-.001925	-.001935	-.000074	-.000000
d2,-2$\overline{d2}$,2	-.001925	-.001935	-.000074	-.000000
d2,0$\overline{2s}$	-.000048	-.000047	-.000000	-.000000
d2,0$\overline{d2}$,0	-.001878	-.001888	-.000073	-.000000
2s$\overline{d2}$,0	-.000000	.000000	.000000	.000000
p2,0$\overline{p3}$,0	-.001434	-.001442	-.000059	-.000000
p3,0$\overline{p2}$,0	-.001434	-.001442	-.000059	-.000000
p2,1$\overline{p3}$,-1	.001434	.001442	.000059	.000000
p3,1$\overline{p2}$,-1	.001434	.001442	.000059	.000000
p2,-1$\overline{p3}$,1	.001434	.001442	.000059	.000000
p3,-1$\overline{p2}$,1	.001434	.001442	.000059	.000000
s4$\overline{s4}$	.001414	.001422	.000058	.000000
2s$\overline{d3}$,0	-.000000	.000000	.000000	-.000000
d3,$\overline{02s}$	-.000000	.000000	-.000000	.000000
p2,0$\overline{p4}$,0	-.000604	-.000608	-.000025	-.000000
p4,0$\overline{p2}$,0	-.000604	-.000608	-.000025	-.000000
p2,1$\overline{p4}$,-1	-.000604	.000608	.000025	.000000

TABLE 11 continued

Eigenvalues			
N_k^2	.916971		.916971
k	5		6
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{1s2s}$	.999998	1s2s	.999998
$\overline{p1,0p2,0}$	-.001082	p1,0p2,0	-.001082
$\overline{p1,1p2,-1}$	.001082	p1,1p2,-1	.001082
$\overline{p2,1p1,-1}$	-.001082	p2,1p1,-1	-.001082
Eigenvalues			
N_k^2	.026999		.026999
k	7		8
Basis Determinants	Coefficients	Basis Determinants	Coefficients
1sp1,0	.999751	$\overline{1sp1,0}$	.999751
2sp2,0	.013450	$\overline{2sp2,0}$	.013450
2sp1,0	-.016273	$\overline{2sp1,0}$	-.016273
2sp3,0	.000177	$\overline{2sp3,0}$	.000177
1sp2,0	-.006302	$\overline{1sp2,0}$	-.006302
2sp4,0	.000073	$\overline{2sp4,0}$	.000073
1sp5,0	-.003429	$\overline{1sp5,0}$	-.003429
Eigenvalues			
N_k^2	.026999		.026999
k	9		10
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{1sp1,-1}$	.999751	1sp1,1	.999751
$\overline{2sp2,-1}$	.013450	2sp2,1	.013450
$\overline{2sp1,-1}$	-.016273	2sp1,1	-.016273
$\overline{2sp3,-1}$	.000177	2sp3,1	.000177

TABLE 11 continued

Eigenvalues N_k^2	.026999		.026999
k continued	9		10
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{1sp2,-1}$	-.006302	1sp2,1	-.006302
$\overline{2sp4,-1}$	.000073	2sp4,1	.000073
$\overline{1sp5,-1}$	-.003429	1sp5,1	-.003429
Eigenvalues N_k^2	.026999		.026999
k	11		12
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{1sp1,1}$	.999751	1sp1,-1	.999751
$\overline{2sp2,1}$	.013450	2sp2,-1	.013450
$\overline{2sp1,1}$	-.016273	2sp1,-1	-.016273
$\overline{2sp3,1}$	.000177	2sp3,-1	.000177
$\overline{1sp2,1}$	-.006302	1sp2,-1	-.006302
$\overline{2sp4,1}$	.000073	2sp4,-1	.000073
$\overline{1sp5,1}$	-.003429	1sp5,-1	-.003429
Eigenvalues N_k^2	.026999		.026999
k	13		14
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$1s\overline{p1,-1}$	.706960	$1s\overline{p1,1}$	.706960
$\overline{1s}p1,-1$	-.706902	$\overline{1s}p1,1$	.706902
$2sp\overline{2,-1}$	.009510	$2sp\overline{2,1}$	.009510
$\overline{2s}p2,-1$	-.009510	$\overline{2s}p2,1$	.009510
$\overline{2s}p1,-1$	-.011507	$2s\overline{p1,1}$	-.011507
$2s\overline{p1,-1}$	.011506	$\overline{2s}p1,1$	-.011506

TABLE 11 continued

Eigenvalues			
N_k^2	.026999		.026999
k continued	13		14
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$2s\overline{p3},-\overline{1}$	.000125	$2s\overline{p3},\overline{1}$	.000125
$\overline{2s}p3,-1$	-.000125	$\overline{2s}p3,1$	.000125
$1s\overline{p2},-\overline{1}$	-.004456	$1s\overline{p2},\overline{1}$	-.004456
$\overline{1s}p2,-1$	.004456	$\overline{1s}p2,1$	-.004456
$2s\overline{p4},-\overline{1}$	.000052	$2s\overline{p4},\overline{1}$	.000052
$\overline{2s}p4,-1$	-.000052	$\overline{2s}p4,1$	.000052
$1s\overline{p5},-\overline{1}$	-.002425	$1s\overline{p5},\overline{1}$	-.002425
$\overline{1s}p5,-1$	.002425	$\overline{1s}p5,1$	-.002425
Eigenvalues			
N_k^2	.026990		.026990
k	15		16
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$1s\overline{p1},-\overline{1}$	.706960	$1s\overline{p1},\overline{1}$	-.706960
$\overline{1s}p1,-1$	.707018	$\overline{1s}p1,1$	.707018
$2s\overline{p2},-\overline{1}$	-.000299	$2s\overline{p2},\overline{1}$	.000299
$\overline{2s}p2,-1$	-.000298	$\overline{2s}p2,1$	-.000298
$\overline{2s}p1,-1$	-.011751	$2s\overline{p1},\overline{1}$	.011751
$2s\overline{p1},-\overline{1}$	-.011752	$\overline{2s}p1,1$	-.011752
$2s\overline{p3},-\overline{1}$	-.000004	$2s\overline{p3},\overline{1}$	.000004
$\overline{2s}p3,-1$	-.000004	$\overline{2s}p3,1$	-.000004
$1s\overline{p2},-\overline{1}$	-.004722	$1s\overline{p2},\overline{1}$	.004722
$\overline{1s}p2,-1$	-.004722	$\overline{1s}p2,1$	-.004722
$2s\overline{p4},-\overline{1}$	-.000002	$2s\overline{p4},\overline{1}$	.000002
$\overline{2s}p4,-1$	-.000002	$\overline{2s}p4,1$	-.000002
$1s\overline{p5},-\overline{1}$	-.002425	$1s\overline{p5},\overline{1}$	.002425
$\overline{1s}p5,-1$	-.002426	$\overline{1s}p5,1$	-.002426

TABLE 11 continued

Eigenvalues			
N_k^2	.026999		.026990
k	17		18
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$1s\overline{p1,0}$	.706960	$1s\overline{p1,0}$	-.706960
$p1,\overline{0}\overline{1s}$	.706902	$p1,\overline{0}\overline{1s}$	.707018
$2s\overline{p2,0}$	.009510	$2s\overline{p2,0}$	.000299
$p2,\overline{0}\overline{2s}$	.009510	$p2,\overline{0}\overline{2s}$	-.000298
$2s\overline{p1,0}$	-.011506	$2s\overline{p1,0}$	-.011752
$p1,\overline{0}\overline{2s}$	-.011507	$p1,\overline{0}\overline{2s}$	.011751
$2s\overline{p3,0}$	.000125	$2s\overline{p3,0}$	.000004
$p3,\overline{0}\overline{2s}$	.000125	$p3,\overline{0}\overline{2s}$	-.000004
$1s\overline{p2,0}$	-.004456	$1s\overline{p2,0}$	.004722
$p2,\overline{0}\overline{1s}$	-.004456	$p2,\overline{0}\overline{1s}$	-.004722
$2s\overline{p4,0}$	.000052	$2s\overline{p4,0}$	.000002
$p4,\overline{0}\overline{2s}$	.000052	$p4,\overline{0}\overline{2s}$	-.000002
$1s\overline{p5,0}$	-.002425	$1s\overline{p5,0}$	.002425
$p5,\overline{0}\overline{1s}$	-.002425	$p5,\overline{0}\overline{1s}$	-.002426
Eigenvalues			
N_k^2	.000691		.000691
k	19		20
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$s1\overline{2s}$	.947170	$2ss\overline{1}$	.947170
$s2\overline{2s}$	-.262170	$2ss\overline{2}$	-.262170
$s3\overline{2s}$	.118995	$2ss\overline{4}$	.118995
$s4\overline{2s}$	.018178	$2ss\overline{3}$	.018178
$s1\overline{1s}$	.140163	$1ss\overline{1}$	.140163

TABLE 11 continued

Eigenvalues			
N_k^2	.000691		.000691
k	21		22
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{2ss1}$	.947170	2ss1	.947170
$\overline{2ss2}$	-.262170	2ss2	-.262170
$\overline{2ss4}$	.118995	2ss4	.118995
$\overline{2ss3}$	.018178	2ss3	.018178
$\overline{1ss1}$	.140163	1ss1	.140163
Eigenvalues			
N_k^2	.000268		.000268
k	23		24
Basis Determinants	Coefficients	Basis Determinants	Coefficients
1sp1,0	-.008878	$\overline{1sp1,0}$	-.008878
2sp2,0	.958222	$\overline{2sp2,0}$	.958222
2sp1,0	.198918	$\overline{2sp1,0}$	.198918
2sp3,0	.151490	$\overline{2sp3,0}$	.151490
1sp2,0	.127731	$\overline{1sp2,0}$	.127731
2sp4,0	.053840	$\overline{2sp4,0}$	.053840
1sp5,0	.000314	$\overline{1sp5,0}$	.000314
Eigenvalues			
N_k^2	.000255		.000255
k	25		26
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{1sp1,-1}$	-.008878	1sp1,1	-.008878
$\overline{2sp2,-1}$	.958222	2sp2,1	.958222
$\overline{2sp1,-1}$	.198918	2sp1,1	.198918
$\overline{2sp3,-1}$	.151490	2sp3,1	.151490
$\overline{1sp2,-1}$	.127731	1sp2,1	.127731

TABLE 11 continued

Eigenvalues			
N_k^2	.000255		.000255
k continued	25		26
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{2sp4,-1}$	.053840	2sp4,1	.053840
$\overline{1sp5,-1}$	.000314	1sp5,1	.000314
Eigenvalues			
N_k^2	.000268		.000268
k	27		28
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{1sp1,1}$	-.008876	1sp1,-1	-.008878
$\overline{2sp2,1}$	.958198	2sp2,-1	.958209
$\overline{2sp1,1}$	.199037	2sp1,-1	.198917
$\overline{2sp3,1}$	.151485	2sp3,-1	.151484
1sp2,1	.127728	1sp2,-1	.127737
$\overline{2sp4,1}$	.053838	2sp4,-1	.053838
$\overline{1sp5,1}$	.000314	1sp5,-1	.000314
Eigenvalues			
N_k^2	.000273		.000273
k	29		30
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$1sp\overline{1,-1}$	.003545	$1sp\overline{1,1}$	-.003540
$\overline{1sp1,-1}$	.003545	$\overline{1sp1,1}$	.003550
$2sp\overline{2,-1}$	.672664	$2sp\overline{2,1}$	-.673205
$\overline{2sp2,-1}$	.672605	$\overline{2sp2,1}$	.672053
$2sp\overline{1,-1}$	.152588	$2sp\overline{1,1}$	-.152702
$\overline{2sp1,-1}$	.152576	$\overline{2sp1,1}$	.152461
$2sp\overline{3,-1}$	.105343	$2sp\overline{3,1}$	-.105425

TABLE 11 continued

Eigenvalues N_k^2	.000273		.000273
k continued	29		30
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$\overline{2s}p3,-1$	.105333	$\overline{2s}p3,1$	.105246
$1s\overline{p2},-1$	.108477	$1s\overline{p2},1$	-.108557
$\overline{1s}p2,-1$	.108470	$\overline{1s}p2,1$	.108403
$2s\overline{p4},-1$	.037495	$2s\overline{p4},1$	-.037524
$\overline{2s}p4,-1$	.037491	$2s\overline{p4},1$	.037460
$1s\overline{p5},-1$	-.000124	$1s\overline{p5},1$	.000124
$\overline{1s}p5,-1$	-.000124	$\overline{1s}p5,1$	-.000124
Eigenvalues N_k^2	.000268		.000268
k	31		32
Basis Determinants	Coefficients	Basis Determinants	Coefficients
$1s\overline{p1},-1$	-.006278	$1s\overline{p1},1$	-.006280
$\overline{1s}p1,-1$	.006278	$\overline{1s}p1,1$	-.006275
$2s\overline{p2},-1$	.677536	$2s\overline{p2},1$	.676979
$\overline{2s}p2,-1$	-.677594	$\overline{2s}p2,1$	.678142
$2s\overline{p1},-1$	.140649	$2s\overline{p1},1$	.140525
$\overline{2s}p1,-1$	-.140663	$\overline{2s}p1,1$	.140787
$2s\overline{p3},-1$	.107114	$2s\overline{p3},1$	.107024
$\overline{2s}p3,-1$	-.107125	$\overline{2s}p3,1$	.107210
$1s\overline{p2},-1$	.090315	$1s\overline{p2},1$	.090234
$\overline{1s}p2,-1$	-.090325	$\overline{1s}p2,1$	.090408
$2s\overline{p4},-1$	.038069	$2s\overline{p4},1$	.038034
$\overline{2s}p4,-1$	-.038072	$\overline{2s}p4,1$	.038105
$1s\overline{p5},-1$	.000222	$1s\overline{p5},1$	.000222
$\overline{1s}p5,-1$	-.000222	$\overline{1s}p5,1$	.000222

TABLE 11 continued

Eigenvalues N_k^2	.000273	.000268
k	33	34

Basis Determinants	Coefficients	Basis Determinants	Coefficients
$1s\overline{p1,0}$	-.003550	$1s\overline{p1,0}$	-.006275
$p1,0\overline{1s}$	.003542	$p1,0\overline{1s}$	-.006279
$2s\overline{p2,0}$	-.672071	$2s\overline{p2,0}$	.678124
$p2,0\overline{2s}$	.673178	$p2,0\overline{2s}$	.676989
$2s\overline{p1,0}$	.152790	$2s\overline{p1,0}$	.140614
$p1,0\overline{2s}$	-.152466	$p1,0\overline{2s}$	.140782
$2s\overline{p3,0}$	-.105249	$2s\overline{p3,0}$	.107208
$p3,0\overline{2s}$	.105423	$p3,0\overline{2s}$	.107028
$1s\overline{p2,0}$	-.108398	$1s\overline{p2,0}$	.090411
$p2,0\overline{1s}$	.108546	$p2,0\overline{1s}$	.090227
$2s\overline{p4,0}$	-.037461	$2s\overline{p4,0}$	.038102
$p4,0\overline{2s}$	.037523	$p4,0\overline{2s}$	.038038
$1s\overline{p5,0}$	.000124	$1s\overline{p5,0}$	.000222
$p5,0\overline{1s}$	-.000124	$p5,0\overline{1s}$	.000222

Basis Determinants	N_k^2 Eigenvalues*	k
1sd1,0	.000066	35
1sd1,1	.000066	36
1sd1,-1	.000066	37
1sd1,2	.000066	38
1sd1,-2	.000066	39
$1s\overline{d1,0}$	.000066	40
$1s\overline{d1,1}$	.000066	41
$1s\overline{d1,-1}$	.000066	42
$1s\overline{d1,2}$	.000066	43
$1s\overline{d1,-2}$	.000066	44

TABLE 11 continued

Basis Determinants	N_k^2 Eigenvalues*	k continued
$\overline{1s}d1,0$	.000066	45
$\overline{1s}d1,1$	.000066	46
$\overline{1s}d1,-1$	.000066	47
$\overline{1s}d1,2$	.000066	48
$\overline{1s}d1,-2$	.000066	49
$1s\overline{d1},0$	.000066	50
$1s\overline{d1},1$	.000066	51
$1s\overline{d1},-1$	.000066	52
$1s\overline{d1},2$	.000066	53
$1s\overline{d1},-2$	.000066	54

* These eigenvalues come from a portion of the second order density matrix which is already in diagonal form. Thus we list only the single basis determinant and its corresponding eigenvalue.

TABLE 12

THE G_k's IN $\Psi = 1/\sqrt{6} \sum_{k=1}^{54} (N_k^2)^{\frac{1}{2}} g_k(1,2) G_k(3,4)$

k	G_k	k	G_k
1	g_1	28	$-g_{27}$
2	$-g_2$	29	g_{32}
3	$-g_3$	30	g_{31}
4	g_4	31	g_{30}
5	$-g_6$	32	g_{29}
6	$-g_5$	33	$-g_{33}$
7	g_8	34	g_{34}
8	g_7	35	g_{50}
9	$-g_{10}$	36	$-g_{52}$
10	$-g_9$	37	$-g_{51}$
11	$-g_{12}$	38	g_{54}
12	$-g_{11}$	39	g_{53}
13	g_{16}	40	$-g_{40}$
14	g_{15}	41	g_{42}
15	g_{14}	42	g_{41}
16	g_{13}	43	$-g_{44}$
17	g_{17}	44	$-g_{43}$
18	$-g_{18}$	45	g_{45}
19	g_{19}	46	$-g_{47}$
20	$-g_{20}$	47	$-g_{46}$
21	g_{22}	48	g_{49}
22	g_{21}	49	g_{48}
23	g_{24}	50	g_{35}
24	g_{23}	51	$-g_{37}$
25	$-g_{26}$	52	$-g_{36}$
26	$-g_{25}$	53	g_{39}
27	$-g_{28}$	54	g_{38}

CHAPTER VI

DISCUSSION OF RESULTS AND CONCLUSIONS

The Symmetry of the Geminals

Table 10 shows the symmetry of the natural geminals, classified according to spin and orbital angular momentum. This symmetry seems to be only approximate in many cases, for example, g_4 is nearly, but not exactly a pure triplet. However, the indications are that if we had diagonalized the complete 124×124 matrix, g_4 would be a pure triplet state. In particular, it was evident after the calculation was completed that the second order density matrix could have been partially diagonalized by resolving it into singlet and triplet blocks. For example, the set of determinants in the original basis belonging to p^2 could have been replaced by the following linear combinations:

$$^1D = 2(0|0) + (1|-1) + (-1|1), \; ^3P = (1|-1) - (-1|1),$$
$$^1S = (0|0) - (1|-1) - (-1|1).$$

They are obtained from their respective principal case starting functions

$$^1D = (1|1), \; ^3P = (1|0), \; ^1S = (0|0)$$

by projecting and using the appropriate step-down operators.

Excited Geminals

We will define three types of original basis geminals as follows:

1. The ground state geminals are those that contain only the Hartree-Fock (1A or 2A) orbitals.

2. The singly excited geminals are those that contain one Hartree-Fock orbital and one other type orbital.

3. The doubly excited geminals are those that contain two orbitals which are not Hartree-Fock.

With these definitions, we can proceed to interpret our results. First, we may examine the natural geminals for the presence of the original basis excited geminals. We note the striking fact that the natural geminals are dominated by ground state geminals and singly excited geminals, and that the doubly excited geminals do not appear with appreciable weight among the first 54 natural geminals in Table 11. Explicitly, all natural geminals with occupation numbers greater than 0.000066 are dominated by geminals containing at least one Hartree-Fock orbital (ground or singly excited geminals) with a weight of at least 0.90. (By weight is meant the sum of the squares of the corresponding coefficients.) The first two natural geminals contain a total weight of ground state geminals of approximately 0.94.

Sinanoğlu (41,42) has discussed the importance of the quadruply excited configurations 6 , 9 , 19 , and 32 in Table 2. A simple Legendre expansion of these configurations shows how the doubly excited geminals are related to them. We feel it may be more meaningful to talk in terms of doubly excited geminals, because the second order density matrix is a fully sufficient basis for discussing correlation

effects. The first two natural geminals g_1 and g_2 have doubly excited original basis geminals occurring with a weight of less than 0.04. In the case of geminals g_3 through g_{54} the weights of doubly excited geminals are less than 2×10^{-6} in any one natural geminal. Natural geminals which are essentially doubly excited have occupation numbers less than 6×10^{-5}.

The Degeneracy of the Geminals

For a non-degenerate geminal g_k, the Schmidt (21) theorem states that $\bar{g}_k = g_k e^{i\alpha}$ with $\alpha = 0$ or π in our case. From Table 12 we see that there is no degeneracy until we reach g_5, which pairs with $-g_6$ in the natural expansion of Ψ. Geminals g_5 through g_{54} are degenerate in sets, within the accuracy of the calculation. We see by comparing Table 10 with Table 12, that the singlets pair with singlets and the triplets with triplets with no pairing between singlets and triplets. This is just what we would expect and verifies the expansion.

A sample calculation containing Ψ_1, Ψ_2, Ψ_3, Ψ_4 showed degeneracy between the natural geminals g_1 and g_2, but this degeneracy was resolved in the complete 37-configuration problem. A thorough study should be made of the symmetry properties of natural geminals.

Correlation Effects

Let us examine the simple case of the Hartree-Fock geminals in order to have a basis for the discussion of correlation effects. In this case the wave function is approximated by a single Slater determinant, and we write:

$$\Psi = (4!)^{-1/2} \,|\, 1\alpha\ 1\bar{\alpha}\ 2\alpha\ 2\bar{\alpha} \,|\qquad (6.1)$$

The simple Legendre expansion of (6.1) gives the Carlson-Keller (16) two-two expansion:

$$\Psi = 6^{-1/2}\,(g_1 g_2 + g_2 g_1 + g_3 g_4 + g_4 g_3 - g_5 g_6 - g_6 g_5)$$

where

$$g_1 = 2^{-1/2}|1\alpha\ 1\bar{\alpha}|\ ,\quad g_2 = 2^{-1/2}|2\alpha\ 2\bar{\alpha}|\ ,\quad g_3 = 2^{-1/2}|1\alpha\ 2\bar{\alpha}|\ ,$$
$$g_4 = 2^{-1/2}|\bar{1}\alpha\ 2\alpha|\ ,\quad g_5 = 2^{-1/2}|1\alpha\ \bar{2}\alpha|\ ,\quad g_6 = 2^{-1/2}|1\alpha\ 2\alpha|\ ,$$
$$g_1 g_2 = g_1(1,2)\, g_2(3,4)\ ,$$

and all the eigenvalues N_i^2 are equal to one. Now the second order density matrix is written:

$$D^2(1,2|1',2') = \binom{4}{2}\int \Psi\,\Psi^{*\prime}\, d\chi_3\, d\chi_4$$
$$= g_1 g_1^{*\prime} + g_2 g_2^{*\prime} + g_3 g_3^{*\prime} + g_4 g_4^{*\prime} + g_5 g_5^{*\prime} + g_6 g_6^{*\prime}. \qquad (6.2)$$

Let us look at the probability distribution for pairs of electrons having the same spin coordinate, $\sigma_1 = \sigma_2$. From equation (6.2) we may write:

$$D^2(1,2|1,2)_{\sigma_1=\sigma_2} = D^2(r_1\sigma_1, r_2\sigma_2|r_1\sigma_1, r_2\sigma_2)_{\sigma_1=\sigma_2}$$
$$= (g_6)^2 = (1/2)\,|1\alpha\ 2\alpha|^2 = 2^{-1}\left\{|1\alpha(1)\ 2\alpha(2)| - |1\alpha(2)\ 2\alpha(1)|\right\}^2$$

so that D^2 vanishes quadratically as $r_1 \to r_2$. This phenomenon may be called the "Fermi hole" (43,44), which is the tendency, due to the antisymmetry of Ψ , for electrons with parallel spin to avoid each other.

Now what happens to the probability distribution D^2 when $r_1 \to r_2$ in general? In order to discuss this case, we make the unitary transformation on the Hartree-Fock g_k set which decomposes the set into singlet and triplet terms. The transformation is written:

$$h_1 = (g_1 + g_2)\, 2^{-1/2} \qquad \text{singlet}$$

$$h_2 = (g_1 - g_2)\, 2^{-1/2} \qquad \text{singlet}$$

$$h_3 = (g_3 - g_4)\, 2^{-1/2} \qquad \text{singlet}$$

$$h_4 = (g_3 + g_4)\, 2^{-1/2} \qquad \text{triplet}$$

$$h_5 = (g_5 - g_6)\, 2^{-1/2} \qquad \text{triplet}$$

$$h_6 = (g_5 + g_6)\, 2^{-1/2} \qquad \text{triplet}.$$

We see that

$$D^2(1,2\,|\,1',2') = \sum_i h_i(1,2)\, h_i^*(1',2') \,.$$

Since the triplet terms are antisymmetric in space, they vanish as $r_1 \to r_2$. Now, let us look at Table 10. This table shows that of the first 54 g_k's thirty-nine are triplet and fifteen are singlet. Thus, thirty-nine of them are vanishing as $r_1 \to r_2$. However, the sum of the occupation numbers of singlet geminals is the same (to the order of accuracy of the calculation) as the occupation numbers of the triplet geminals in Watson's wave function. If a second order density matrix were to be constructed so that the triplet geminals have larger occupation numbers than the singlet geminals, it would approach more nearly the desired property of becoming small as $r_1 \to r_2$. However, such a density matrix may not be N-representable by a singlet wave function.

The essential improvement in Watson's wave function over the Hartree-Fock wave function is the effect of correlation on electrons of paired spin, for the Fermi hole, as we have said, keeps electrons of parallel spin apart. This improvement should show up in the occupation numbers and the form of the singlet natural geminals. Correlation causes a depression of the occupation numbers of the natural spin-orbitals (natural 1-states) below one, so one might expect a similar depression in the occupation numbers of the natural two-states. Explicitly, one might have expected N_1^2 , N_2^2 , and N_3^2 , the occupation numbers of the singlet geminals (which had occupation numbers equal to one in the Hartree-Fock case) all to be depressed, and perhaps N_4^2 , N_5^2 , and N_6^2 , the triplet geminals to be depressed less, or even to increase above one. However, just the opposite has happened. The three geminals of largest occupation number are all singlets. The first is even slightly greater than one. On the other hand, the form of the first three geminals is changed, with some angular correlation appearing. Furthermore, the original orthonormal basis orbitals have nodes, and it would be of interest to examine the behavior of the natural geminals as $r_1 \rightarrow r_2$.

We note that the geminals g_7 through g_{18} have fairly large N_k^2's compared to g_{19} through g_{54} . The former geminals represent the $2s$-$2p$ orbital degeneracy referred to by Watson (15).

Conclusions

It is apparent that the geminal expansion for Be is very valuable for explaining, interpreting and comparing the Be wave functions and probably wave functions for other even numbered systems. We hope that the calculation of natural geminals for complicated wave functions will

help in the search for the necessary and sufficient conditions for the second order density matrix to be N-representable. Future investigations will examine this possibility, and more calculations will be made of the second order density matrix for various wave functions.

CHAPTER VII

SUMMARY

The first and second order density matrices have been calculated from Watson's (15) wave function for the Be atom. A general program in Fortran was developed to calculate the second order density matrix for systems with up to twenty fermions.

Two theorems were given for the ^1S projection of four electron configurations.

The first and second order density matrices were diagonalized, giving the natural $\mathbf{1}$-states and the natural $\mathbf{2}$-states respectively. We have shown the electron distribution from the natural $\mathbf{1}$-states, and we calculated the Carlson-Keller (16) two-two expansion of the wave function from the natural $\mathbf{2}$-states.

The simplicity and beauty of the natural geminal expansion of the wave function were striking. We have shown how natural geminals can be resolved into singlets and triplets, and how the natural geminal expansion of D^2 converges rapidly in 54 terms having a trace of 5.999099, compared to the complete 594 term expansion, having a trace of 5.9999896.

We have discussed correlation effects in terms of geminals and the exact form of the wave function as indicated by the depression of the occupation numbers.

This work contains the first calculation, known to the author, of a second order density matrix for a system containing more than two electrons, represented by a wave function containing a large number of configurations.

APPENDICES

APPENDIX I

THE SECOND ORDER DENSITY MATRIX*

Truncated 50 x 50 Block

	$1s\overline{1s}$	$2s\overline{2s}$	$1s\overline{2s}$	$2s\overline{1s}$	$p1,0\overline{p1,0}$
$1s\overline{1s}$	.4996114				
$2s\overline{2s}$	.0002647	.4092614			
$1s\overline{2s}$	-.0006672	.0000988	.4085143		
$2s\overline{1s}$	-.0006672	.0000988	.0000305	.4085143	
$p1,0\overline{p1,0}$	-.0005256	-.0787271	-.0013014	-.0013014	.0135080
$p1,1\overline{p1,-1}$	.0005256	.0787271	.0013014	.0013014	-.0135080
$p1,-1\overline{p1,1}$	.0005256	.0787265	.0013014	.0013014	-.0135079
$s1\overline{s1}$	-.0119400	-.0000054	.0018757	.0018757	.0000023
$p2,0\overline{p2,0}$	-.0078280	-.0000891	.0009363	.0009363	.0000177
$p2,1\overline{p2,-1}$	.0078280	.0000891	-.0009363	-.0009363	-.0000177
$p2,-1\overline{p2,1}$	.0078280	.0000891	-.0009363	-.0009363	-.0000177
$d1,0\overline{d1,0}$	-.0000000	-.0039060	-.0000003	-.0000003	.0006699
$d1,1\overline{d1,-1}$	.0000000	.0039060	.0000003	.0000003	-.0006699
$d1,-1\overline{d1,1}$	.0000000	.0039060	.0000003	.0000003	-.0006699
$d1,2\overline{d1,-2}$	-.0000000	-.0039060	-.0000003	-.0000003	.0006699
$d1,-2\overline{d1,2}$	-.0000000	-.0039060	-.0000003	-.0000003	.0006699
$s1\overline{s2}$	.0034838				-.0000040
$s2\overline{s1}$	.0034838				-.0000040
$p1,0\overline{p2,0}$	-.0014426	.0005033	.0004962	.0009924	-.0000882
$p2,0\overline{p1,0}$	-.0014426	.0005033	.0009924	.0004962	-.0000882
$p1,1\overline{p2,-1}$	.0014426	-.0005033	-.0004962	-.0009924	.0000882
$p2,1\overline{p1,-1}$	.0014426	-.0005033	-.0009924	-.0004962	.0000882
$p1,-1\overline{p2,1}$	.0014426	-.0005033	-.0004962	-.0009924	.0000882
$p2,-1\overline{p1,1}$	.0014426	-.0005033	-.0009924	-.0004962	.0000882
$s3\overline{s4}$	-.0019461				.0000022
$s4\overline{s3}$	-.0019461				.0000022
$s1\overline{s4}$	-.0016700				.0000019
$s4\overline{s1}$	-.0016700				.0000019

APPENDIX I continued

Truncated 50 x 50 Block

	$1s\overline{1s}$	$2s\overline{2s}$	$1s\overline{2s}$	$2s\overline{1s}$	$p1,0\overline{p1,0}$
$p3,0\overline{p3,0}$	-.0014219				.0000016
$p3,1\overline{p3,-1}$	.0014219				-.0000016
$p3,-1\overline{p3,1}$	.0014219				-.0000016
$d2,1\overline{d2,-1}$	.0013642	.0000007	-.0000017	-.0000017	-.0000014
$d2,-1\overline{d2,1}$	.0013642	.0000007	-.0000017	-.0000017	-.0000014
$d2,2\overline{d2,-2}$	-.0013642	-.0000007	.0000017	.0000017	.0000014
$d2,-2\overline{d2,2}$	-.0013642	-.0000007	.0000017	.0000017	.0000014
$d2,0\overline{2s}$	-.0000336	-.0000002	.0000006	.0000006	
$d2,0\overline{d2,0}$	-.0013306	-.0000004	.0000011	.0000011	.0000014
$p2,0\overline{p3,0}$	-.0010162				.0000012
$p3,0\overline{p2,0}$	-.0010162				.0000012
$p2,1\overline{p3,-1}$	.0010162				-.0000012
$p3,1\overline{p2,-1}$	.0010162				-.0000012
$p2,-1\overline{p3,1}$	.0010162				-.0000012
$p3,-1\overline{p2,1}$	.0010162				-.0000012
$s4\overline{s4}$	.0010020				-.0000011
$p2,0\overline{p4,0}$	-.0004283				.0000005
$p4,0\overline{p2,0}$	-.0004283				.0000005
$p2,1\overline{p4,-1}$	.0004283				-.0000005

Truncated 50 x 50 Block

	$p1,1\overline{p1,-1}$	$p1,-1\overline{p1,1}$	$s1\overline{s1}$	$p2,0\overline{p2,0}$	$p2,1\overline{p2,-1}$
$p1,1\overline{p1,-1}$	.0135080				
$p1,-1\overline{p1,1}$	.0135079	.0135080			
$s1\overline{s1}$	-.0000023	-.0000023	.0003016		
$p2,0\overline{p2,0}$	-.0000177	-.0000177	.0001950	.0001266	
$p2,1\overline{p2,-1}$	.0000177	.0000177	-.0001950	-.0001266	.0001266
$p2,-1\overline{p2,1}$	.0000177	.0000177	-.0001950	-.0001266	.0001266
$d1,0\overline{d1,0}$	-.0006699	-.0006699			
$d1,1\overline{d1,-1}$	.0006699	.0006699			

APPENDIX I continued

Truncated 50 x 50 Block

	p1,1$\overline{\text{p1,-1}}$	p1,-1$\overline{\text{p1,1}}$	s1$\overline{\text{s1}}$	p2,0$\overline{\text{p2,0}}$	p2,1$\overline{\text{p2,-1}}$
d1,-1$\overline{\text{d1,1}}$	.0006699	.0006699			
d1,2$\overline{\text{d1,-2}}$	-.0006699	-.0006699			
d1,-2$\overline{\text{d1,2}}$	-.0006699	-.0006699			
s1$\overline{\text{s2}}$			-.0000846	-.0000551	.0000551
s2$\overline{\text{s1}}$			-.0000846	-.0000551	.0000551
p1,0$\overline{\text{p2,0}}$	.0000882	.0000882	.0000410	.0000257	-.0000257
p2,0$\overline{\text{p1,0}}$	.0000882	.0000882	.0000410	.0000257	-.0000257
p1,1$\overline{\text{p2,-1}}$	-.0000882	-.0000882	-.0000410	-.0000257	.0000257
p2,1$\overline{\text{p1,-1}}$	-.0000882	-.0000882	-.0000410	-.0000257	.0000257
p1,-1$\overline{\text{p2,1}}$	-.0000882	-.0000882	-.0000410	-.0000257	.0000257
p2,-1$\overline{\text{p1,1}}$	-.0000882	-.0000882	-.0000410	-.0000257	.0000257
s3$\overline{\text{s4}}$			.0000473	.0000308	-.0000308
s4$\overline{\text{s3}}$			.0000473	.0000308	-.0000308
s1$\overline{\text{s4}}$			.0000406	.0000264	-.0000264
s4$\overline{\text{s1}}$			.0000406	.0000264	-.0000264
p3,0$\overline{\text{p3,0}}$			.0000345	.0000225	-.0000225
p3,1$\overline{\text{p3,-1}}$			-.0000345	-.0000225	.0000225
p3,-1$\overline{\text{p3,1}}$			-.0000345	-.0000225	.0000225
d2,1$\overline{\text{d2,-1}}$			-.0000327	-.0000214	.0000214
d2,-1$\overline{\text{d2,1}}$			-.0000327	-.0000214	.0000214
d2,2$\overline{\text{d2,-2}}$			.0000327	.0000214	-.0000214
d2,-2$\overline{\text{d2,2}}$			.0000327	.0000214	-.0000214
d2,0$\overline{\text{2s}}$			.0000007	.0000005	-.0000005
d2,0$\overline{\text{d2,0}}$			.0000320	.0000209	-.0000209
p2,0$\overline{\text{p3,0}}$			.0000247	.0000161	-.0000161
p3,0$\overline{\text{p2,0}}$			.0000247	.0000161	-.0000161
p2,1$\overline{\text{p3,-1}}$			-.0000247	-.0000161	.0000161
p3,1$\overline{\text{p2,-1}}$			-.0000247	-.0000161	.0000161
p2,-1$\overline{\text{p3,1}}$			-.0000247	-.0000161	.0000161
p3,-1$\overline{\text{p2,1}}$			-.0000247	-.0000161	.0000161

APPENDIX I continued

Truncated 50 x 50 Block

	p1,1$\overline{\text{p1}}$,-1	p1,-1$\overline{\text{p1}}$,1	s1$\overline{\text{s1}}$	p2,0$\overline{\text{p2}}$,0	p2,1$\overline{\text{p2}}$,-1
s4$\overline{\text{s4}}$			-.0000243	-.0000158	.0000158
p2,0$\overline{\text{p4}}$,0			.0000104		
p4,0$\overline{\text{p2}}$,0			.0000104		
p2,1$\overline{\text{p4}}$,-1			-.0000104		

Truncated 50 x 50 Block

	p2,-1$\overline{\text{p2}}$,1	d1,0$\overline{\text{d1}}$,0	d1,1$\overline{\text{d1}}$,-1	d1,-1$\overline{\text{d1}}$,1	d1,2$\overline{\text{d1}}$,-2
p2,-1$\overline{\text{p2}}$,1	.0001266				
d1,0$\overline{\text{d1}}$,0		.0000332			
d1,1$\overline{\text{d1}}$,-1		-.0000333	.0000332		
d1,-1$\overline{\text{d1}}$,1		-.0000333	.0000333	.0000332	
d1,2$\overline{\text{d1}}$,-2		.0000333	-.0000333	-.0000333	.0000332
d1,-2$\overline{\text{d1}}$,2	-.0000007	.0000333	-.0000333	-.0000333	.0000333
s1$\overline{\text{s2}}$	.0000550				
s2$\overline{\text{s1}}$	.0000550				
p1,0$\overline{\text{p2}}$,0	-.0000257				
p2,0$\overline{\text{p1}}$,0	-.0000257				
p1,1$\overline{\text{p2}}$,-1	.0000257				
p2,1$\overline{\text{p1}}$,-1	.0000257				
p1,-1$\overline{\text{p2}}$,1	.0000257				
p2,-1$\overline{\text{p1}}$,1	.0000257				
s3$\overline{\text{s4}}$	-.0000308				
s4$\overline{\text{s3}}$	-.0000308				
s1$\overline{\text{s4}}$	-.0000264				
s4$\overline{\text{s1}}$	-.0000264				
p3,0$\overline{\text{p3}}$,0	-.0000225				
p3,1$\overline{\text{p3}}$,-1	.0000225				
p3,-1$\overline{\text{p3}}$,1	.0000225				
d2,1$\overline{\text{d2}}$,-1	.0000214				
d2,-1$\overline{\text{d2}}$,1	.0000214				

APPENDIX I continued

Truncated 50 x 50 Block

	p2,-1p2,1	d1,0d1,0	d1,1d1,-1	d1,-1d1,1	d1,2d1,-2
d2,2d2,-2	-.0000214				
d2,-2d2,2	-.0000214				
d2,0d2,0	-.0000209				
p2,0p3,0	-.0000161				
p3,0p2,0	-.0000161				
p2,1p3,-1	.0000161				
p3,1p2,-1	.0000161				
p2,-1p3,1	.0000161				
p3,-1p2,1	.0000161				
s4s4	.0000158				

Truncated 50 x 50 Block

	d1,-2d1,2	s1s2	s2s1	p1,0p2,0	p2,0p1,0
d1,-2d1,2	.0000332				
s1s2		.0000264			
s2s1		.0000265	.0000264		
p1,0p2,0		-.0000110	-.0000110	.0000105	
p2,0p1,0		-.0000110	-.0000110		.0000105
p1,1p2,-1		.0000110	.0000110		
p2,1p1,-1		.0000110	.0000110		
p1,-1p2,1		.0000110	.0000110		
p2,-1p1,1		.0000110	.0000110		
s3s4		-.0000148	-.0000148		
s4s3		-.0000148	-.0000148		
s1s4		-.0000127	-.0000127		
s4s1		-.0000127	-.0000127		
p3,0p3,0		-.0000108	-.0000108		
p3,1p3,-1		.0000108	.0000108		
p3,-1p3,1		.0000108	.0000108		
d2,1d2,-1		.0000096	.0000096		

APPENDIX I continued

Truncated 50 x 50 Block

	d1,-2$\overline{d1,2}$	s1$\overline{s2}$	s2$\overline{s1}$	p1,0$\overline{p2,0}$	p2,0$\overline{p1,0}$
d2,-1$\overline{d2,1}$		.0000096	.0000096		
d2,2$\overline{d2,-2}$		-.0000096	-.0000096		
d2,-2$\overline{d2,2}$		-.0000096	-.0000096		
d2,0$\overline{d2,0}$		-.0000096	-.0000096		

Truncated 50 x 50 Block

	p1,1$\overline{p2,-1}$	p2,1$\overline{p1,-1}$	p1,-1$\overline{p2,1}$	p2,-1$\overline{p1,1}$	s3$\overline{s4}$
p1,1$\overline{p2,-1}$	.0000105				
p2,1$\overline{p1,-1}$		.0000105			
p1,-1$\overline{p2,1}$			.0000105		
p2,-1$\overline{p1,1}$				.0000105	
s3$\overline{s4}$					.0000082

Truncated 50 x 50 Block

	s4$\overline{s3}$	s1$\overline{s4}$	s4$\overline{s1}$	p3,0$\overline{p3,0}$	p3,1$\overline{p3,-1}$
s4$\overline{s3}$	.0000082				
s1$\overline{s4}$		.0000061			
s4$\overline{s1}$			.0000061		

First 4 x 4 Block

	1s2$\overline{s}$	$\overline{p1,0p2,0}$	$\overline{p1,1p2,-1}$	$\overline{p2,1p1,-1}$
1s2$\overline{s}$	.4584839			
$\overline{p1,0p2,0}$	-.0004962	.0000066		
$\overline{p1,1p2,-1}$	.0004962	-.0000005	.0000066	
$\overline{p2,1p1,-1}$	-.0004962	.0000005	-.0000005	.0000066

Second 4 x 4 Block

	1s2s	p1,0p2,0	p1,1p2,-1	p2,1p1,-1
1s2s	.4584839			
p1,0p2,0	-.0004962	.0000066		

APPENDIX I continued

Second 4 x 4 Block

	1s2s	p1,0p2,0	p1,1p2,-1	p2,1p1,-1
p1,1p2,-1	.0004962	-.0000005	.0000066	
p2,1p1,-1	-.0004962	.0000005	-.0000005	.0000066

First 5 x 5 Block

	$s1\overline{2s}$	$s2\overline{2s}$	$s3\overline{2s}$	$s4\overline{2s}$	$s1\overline{1s}$
$s1\overline{2s}$	.0003106				
$s2\overline{2s}$	-.0000846	.0000264			
$s3\overline{2s}$	.0000369	-.0000127	.0000165		
$s4\overline{2s}$	.0000071		-.0000049	.0000088	
$s1\overline{1s}$	.0000452	-.0000142	.0000068		.0000075

Second 5 x 5 Block

	$2ss\overline{1}$	$2ss\overline{2}$	$2ss\overline{4}$	$2ss\overline{3}$	$1ss\overline{1}$
$2ss\overline{1}$	.0003106				
$2ss\overline{2}$	-.0000846	.0000264			
$2ss\overline{4}$	.0000369	-.0000127	.0000165		
$2ss\overline{3}$	.0000071		-.0000049	.0000083	
$1ss\overline{1}$	.0000452	-.0000142	.0000068		.0000075

Third 5 x 5 Block

	$\overline{2ss1}$	$\overline{2ss2}$	$\overline{2ss4}$	$\overline{2ss3}$	$\overline{1ss1}$
$\overline{2ss1}$	.0003106				
$\overline{2ss2}$	-.0000846	.0000264			
$\overline{2ss4}$	.0000369	-.0000127	.0000165		
$\overline{2ss3}$	.0000071		-.0000049	.0000083	
$\overline{1ss1}$	.0000452	-.0000142	.0000068		.0000075

APPENDIX I continued

Fourth 5 x 5 Block

	2ss1	2ss2	2ss4	2ss3	1ss1
2ss1	.0003106				
2ss2	-.0000846	.0000264			
2ss4	.0000369	-.0000127	.0000165		
2ss3	.0000071		-.0000049	.0000083	
1ss1	.0000452	-.0000142	.0000068		.0000075

First 7 x 7 Block

	1sp1,0	2sp2,0	2sp1,0	2sp3,0	1sp2,0
1sp1,0	.0134926				
2sp2,0	.0001804	.0001257			
2sp1,0	-.0002198	.0000226	.0000093		
2sp3,0	.0000022	.0000192	.0000032	.0000066	
1sp2,0	-.0000852	.0000153	.0000050	.0000021	.0000059
2sp4,0	.0000009	.0000070	.0000013	.0000009	.0000009
1sp5,0	-.0000463	-.0000006	.0000008		.0000003

First 7 x 7 Block

	2sp4,0	1sp5,0
2sp4,0	.0000011	
1sp5,0		.0000005

Second 7 x 7 Block

	$\overline{1sp1,0}$	$\overline{2sp2,0}$	$\overline{2sp1,0}$	$\overline{2sp3,0}$	$\overline{1sp2,0}$
$\overline{1sp1,0}$	.0134926				
$\overline{2sp2,0}$	.0001804	.0001257			
$\overline{2sp1,0}$	-.0002198	.0000226	.0000093		
$\overline{2sp3,0}$	.0000022	.0000192	.0000032	.0000066	
$\overline{1sp2,0}$	-.0000852	.0000153	.0000050	.0000021	.0000059
$\overline{2sp4,0}$	.0000009	.0000070	.0000013	.0000009	.0000009
$\overline{1sp5,0}$	-.0000463	-.0000006	.0000008		.0000003

APPENDIX I continued

	Second 7 x 7 Block	
	$\overline{2sp4,0}$	$\overline{1sp5,0}$
$\overline{2sp4,0}$	.0000011	
$\overline{1sp5,0}$		.0000005

	Third 7 x 7 Block				
	$\overline{1sp1,1}$	$\overline{2sp2,1}$	$\overline{2sp1,1}$	$\overline{2sp3,1}$	$\overline{1sp2,1}$
$\overline{1sp1,1}$	.0134926				
$\overline{2sp2,1}$	.0001804	.0001257			
$\overline{2sp1,1}$	-.0002198	.0000226	.0000094		
$\overline{2sp3,1}$	.0000022	.0000192	.0000032	.0000066	
$\overline{1sp2,1}$	-.0000852	.0000153	.0000050	.0000021	.0000059
$\overline{2sp4,1}$	.0000009	.0000070	.0000013	.0000009	.0000009
$\overline{1sp5,1}$	-.0000463	-.0000006	.0000008		.0000003

	Third 7 x 7 Block	
	$\overline{2sp4,1}$	$\overline{1sp5,1}$
$\overline{2sp4,1}$	.0000011	
$\overline{1sp5,1}$		.0000005

	Fourth 7 x 7 Block				
	$\overline{1sp1,-1}$	$\overline{2sp2,-1}$	$\overline{2sp1,-1}$	$\overline{2sp3,-1}$	$\overline{1sp2,-1}$
$\overline{1sp1,-1}$	.0134926				
$\overline{2sp2,-1}$	.0001804	.0001257			
$\overline{2sp1,-1}$	-.0002198	.0000226	.0000093		
$\overline{2sp3,-1}$	.0000022	.0000192	.0000032	.0000066	
$\overline{1sp2,-1}$	-.0000852	.0000153	.0000050	.0000021	.0000059
$\overline{2sp4,-1}$	.0000009	.0000070	.0000013	.0000009	.0000009
1sp5,-1	-.0000463	-.0000006	.0000008		.0000003

	Fourth 7 x 7 Block	
	$\overline{2sp4,-1}$	$\overline{1sp5,-1}$
$\overline{2sp4,-1}$	.0000011	
$\overline{1sp5,-1}$		.0000005

APPENDIX I continued

Fifth 7 x 7 Block

	1sp1,1	2sp2,1	2sp1,1	2sp3,1	1sp2,1
1sp1,1	.0134926				
2sp2,1	.0001803	.0001257			
2sp1,1	-.0002198	.0000226	.0000093		
2sp3,1	.0000022	.0000192	.0000032	.0000066	
1sp2,1	-.0000852	.0000153	.0000050	.0000021	.0000059
2sp4,1	.0000009	.0000070	.0000013	.0000009	.0000009
1sp5,1	-.0000463	-.0000006	.0000008		.0000003

Fifth 7 x 7 Block

	2sp4,1	1sp5,1
2sp4,1	.0000011	
1sp5,1		.0000005

Sixth 7 x 7 Block

	1sp1,-1	2sp2,-1	2sp1,-1	2sp3,-1	1sp2,-1
1sp1,-1	.0134926				
2sp2,-1	.0001804	.0001257			
2sp1,-1	-.0002198	.0000226	.0000093		
2sp3,-1	.0000022	.0000192	.0000032	.0000066	
1sp2,-1	-.0000852	.0000153	.0000050	.0000021	.0000059
2sp4,-1	.0000009	.0000070	.0000013	.0000009	.0000009
1sp5,-1	-.0000463	-.0000006	.0000008		.0000003

Sixth 7 x 7 Block

	2sp4,-1	1sp5,-1
2sp4,-1	.0000011	
1sp5,-1		.0000005

APPENDIX I continued

First 14 x 14 Block

	$1s\overline{p1},-\overline{1}$	$\overline{1s}p1,-1$	$2s\overline{p2},-\overline{1}$	$\overline{2s}p2,-1$	$\overline{2s}p1,-\overline{1}$
$1s\overline{p1},-\overline{1}$	.0134915				
$\overline{1s}p1,-1$	.0000011	.0134915			
$2s\overline{p2},-\overline{1}$	.0000877	.0000927	.0001246		
$\overline{2s}p2,-1$	.0000927	.0000877	.0000011	.0001246	
$\overline{2s}p1,-\overline{1}$	.0000021	-.0002219	-.0000024	.0000250	.0000115
$2s\overline{p1},-\overline{1}$	-.0002219	.0000021	.0000250	-.0000024	-.0000021
$2s\overline{p3},-\overline{1}$	.0000011	.0000011	.0000192		
$\overline{2s}p3,-1$	.0000011	.0000011		.0000192	.0000032
$1s\overline{p2},-\overline{1}$	-.0000876	.0000024	.0000174	-.0000021	-.0000007
$\overline{1s}p2,-1$	.0000024	-.0000876	-.0000021	.0000174	.0000056
$2s\overline{p4},-\overline{1}$	.0000005	.0000005	.0000070		
$\overline{2s}p4,-1$	.0000005	.0000005		.0000070	.0000013
$1s\overline{p5},-\overline{1}$	-.0000463		-.0000003	-.0000003	
$\overline{1s}p5,-1$		-.0000463	-.0000003	-.0000003	.0000008

First 14 x 14 Block

	$2s\overline{p1},-\overline{1}$	$2s\overline{p3},-\overline{1}$	$\overline{2s}p3,-1$	$1s\overline{p2},-\overline{1}$	$\overline{1s}p2,-1$
$2s\overline{p1},-\overline{1}$	.0000114				
$2s\overline{p3},-\overline{1}$	.0000032	.0000066			
$\overline{2s}p3,-1$			.0000066		
$1s\overline{p2},-\overline{1}$	.0000056	.0000021		.0000051	
$\overline{1s}p2,-1$	-.0000007		.0000021	-.0000021	.0000051
$2s\overline{p4},-\overline{1}$	.0000013	.0000009		.0000009	
$\overline{2s}p4,-1$			.0000009		.0000009
$1s\overline{p5},-\overline{1}$	.0000008			.0000003	
$\overline{1s}p5,-1$					.0000003

APPENDIX I continued

First 14 x 14 Block

	$2sp\overline{4,-1}$	$\overline{2s}p4,-1$	$1sp\overline{5,-1}$	$\overline{1s}p5,-1$
$2sp\overline{4,-1}$	.0000011			
$\overline{2s}p4,-1$		.0000011		
$1sp\overline{5,-1}$			.0000005	
$\overline{1s}p5,-1$				.0000005

Second 14 x 14 Block

	$1sp\overline{1,0}$	$p1,0\overline{1s}$	$2sp\overline{2,0}$	$p2,0\overline{2s}$	$2sp\overline{1,0}$
$1sp\overline{1,0}$	.0134915				
$p1,0\overline{1s}$	-.0000011	.0134915			
$2sp\overline{2,0}$	.0000877	-.0000927	.0001246		
$p2,0\overline{2s}$	-.0000927	.0000877	-.0000011	.0001246	
$2sp\overline{1,0}$	-.0002219	-.0000021	.0000250	.0000024	.0000114
$p1,0\overline{2s}$	-.0000021	-.0002219	.0000024	.0000250	.0000021
$2sp\overline{3,0}$	.0000011	-.0000011	.0000192		.0000032
$p3,0\overline{2s}$	-.0000011	.0000011		.0000192	
$1sp\overline{2,0}$	-.0000876	-.0000024	.0000174	.0000021	.0000056
$p2,0\overline{1s}$	-.0000024	-.0000876	.0000021	.0000174	.0000007
$2sp\overline{4,0}$	.0000005	-.0000005	.0000070		.0000013
$p4,0\overline{2s}$	-.0000005	.0000005		.0000070	
$1sp\overline{5,0}$	-.0000463		-.0000003	.0000003	.0000008
$p5,0\overline{1s}$		-.0000463	.0000003	-.0000003	

Second 14 x 14 Block

	$p1,0\overline{2s}$	$2sp\overline{3,0}$	$p3,0\overline{2s}$	$1sp\overline{2,0}$	$p2,0\overline{1s}$
$p1,0\overline{2s}$	.0000114				
$2sp\overline{3,0}$		.0000066			
$p3,0\overline{2s}$	.0000032		.0000066		
$1sp\overline{2,0}$	.0000007	.0000021		.0000051	
$p2,0\overline{1s}$	.0000056		.0000021	.0000021	.0000051
$2sp\overline{4,0}$		.0000009		.0000008	
p4,02s	.0000013		.0000009		.0000009

APPENDIX I continued

Second 14 x 14 Block

	p1,02s	2sp3,0	p3,02s	1sp2,0	p2,01s
1sp5,0				.0000003	
p5,01s	.0000008				.0000003

Second 14 x 14 Block

	2sp4,0	p4,02s	1sp5,0	p5,01s	
2sp4,0	.0000011				
p4,02s		.0000011			
1sp5,0			.0000005		
p5,01s				.0000005	

Third 14 x 14 Block

	1sp1,1	1sp1,1	2sp2,1	2sp2,1	2sp1,1
1sp1,1	.0134915				
1sp1,1	.0000011	.0134915			
2sp2,1	.0000877	.0000927	.0001246		
2sp2,1	.0000927	.0000877	.0000011	.0001246	
2sp1,1	-.0002219	.0000021	.0000250	-.0000024	.0000114
2sp1,1	.0000021	-.0002219	-.0000024	.0000250	-.0000021
2sp3,1	.0000011	.0000011	.0000192		.0000032
2sp3,1	.0000011	.0000011		.0000192	
1sp2,1	-.0000876	.0000024	.0000174	-.0000021	.0000056
1sp2,1	.0000024	-.0000876	-.0000021	.0000174	-.0000007
2sp4,1	.0000005	.0000005	.0000070		.0000013
2sp4,1	.0000005	.0000005		.0000070	
1sp5,1	-.0000463		-.0000003	-.0000003	.0000008
1sp5,1		-.0000463	-.0000003	-.0000003	

APPENDIX I continued

Third 14 x 14 Block

	$\overline{2s}p1,1$	$2s\overline{p3,1}$	$\overline{2s}p3,1$	$1s\overline{p2,1}$	$\overline{1s}p2,1$
$\overline{2s}p1,1$	.0000114				
$2s\overline{p3,1}$		.0000066			
$\overline{2s}p3,1$	.0000032		.0000066		
$1s\overline{p2,1}$	-.0000007	.0000021		.0000051	
$\overline{1s}p2,1$	.0000056		.0000021	-.0000021	.0000051
$2s\overline{p4,1}$		.0000009		.0000009	
$\overline{2s}p4,1$	.0000013		.0000009		.0000009
$1s\overline{p5,1}$				.0000003	
$\overline{1s}p5,1$	.0000008				.0000003

Third 14 x 14 Block

	$2s\overline{p4,1}$	$\overline{2s}p4,1$	$1s\overline{p5,1}$	$\overline{1s}p5,1$
$2s\overline{p4,1}$	.0000011			
$\overline{2s}p4,1$		.0000011		
$1s\overline{p5,1}$			.0000005	
$\overline{1s}p5,1$				.0000005

* Most matrix elements less than .000001 have been eliminated from the truncated 50 x 50 block. The other blocks have all terms present. The basis determinants in all the blocks are not normalized.

APPENDIX II

THE FORTRAN PROGRAM TO CALCULATE THE SECOND ORDER DENSITY MATRIX

This program consists of four chains, all stored on Tape 3. They are described as follows:

1. Chain (4,3) is the first chain stored on Tape 3, and it consists of a restart routine for restarting the program in the event that the machine fails. The restart program is not ordinarily used, so that most of the time this program serves only to initialize IZP , where IZP is one, if the job is just starting, or the job is to start from the beginning. This chain is ordinarily used only once.

If the machine fails at any time during a run, except during a crucial period which is printed on line as (WRITING TAPE 2), (END OF WRITING TAPE 2), then the program can be restarted without the loss of any partial results by (1) erasing the memory, (2) depressing sense switch 1, and (3) feeding the program into the machine through the card reader. When this is done, the machine prints on line (NUM1 = the number of the Slater determinants), (NUM2 = the order of the Slater determinants), (IDZ = the cycle where the machine will begin calculating), and (ANORM = the normalization constant calculated by the machine). These print outs serve as a check that the program is restarting properly. This chain ends by calling chain (1,3) into the memory of the machine.

2. Chain (1,3) is the second chain stored on Tape 3, and it consists of a read input routine which reads the number of Slater determinants (NUM1) , and the order of Slater determinants (NUM2) on the first card in format (2I3) . It then reads the subsequent cards in format (E20.8, 4I3) . These cards contain the coefficients in the first twenty columns with exponent, and the corresponding Slater determinants coded as integers $k_1 < k_2 < k_3 < k_4$ in the next twelve columns. The format (4I3) should be changed for systems containing more than four fermions or less than four fermions.

The input data are stored on Tape 2 in this chain. This chain also prints on line (I = the cycle number) . The cycle number is the number of the Slater determinant which is being compared with the other Slater determinants.

The chain continues by comparing the first four k's with the rest of the set of four k's . Thus comparison results in the finding of all the minors obtainable with proper coefficients. Whenever a non-vanishing minor is found the proper factor + 1 or - 1 is determined and the proper coefficients found for each non-vanishing minor. A test is made in the chain to determine whether a minor belongs to the upper or lower triangular portion of the second order density matrix, and the minor is always placed in the upper triangular portion of the matrix, the indices being changed if necessary. Minors having identical k's are added. If the number of minors calculated in this chain exceeds a thousand, the program prints (OVERFLOW DIMENSION 1000 IN KTERM) , and exits. The chain ends by calling chain (2,3) into the memory of the machine.

3. Chain (2,3) is the third chain stored on Tape 3, and it starts by ordering the minors so that they are stored by rows commencing with the $k_1 = 1$, $k_2 = 2$ row if it exists. It continues by increasing the cycle number I by 1 and ends by calling chain (3,3) into the memory of the machine.

4. Chain (4,3) is the fifth and last chain stored on Tape 3, and it starts by printing, (SUB TRAN) on line. Tapes 7 or 4 are used as intermediate storage in this chain so that the memory of the machine will not be overloaded. If the job is a restart job, the chain prints (PUSH SENSE SWITCH 1 UP), (PRESS START) then pauses until start is pressed. If the job is not a restart job, chain (4,3) bypasses the restart routine.

The chain continues by combining all the minors with identical k's and storing the minors with their corresponding coefficients by rows starting with $k_1 = 1$, $k_2 = 2$ row if it exists. The minors are stored in blocks of a thousand on either Tape 7 or Tape 4, depending upon the cycle. The other tape is used as the input data tape to this chain. The tapes alternate from cycle to cycle as input data tapes and storage tapes. All information is read or written in blocks of a thousand on these tapes to eliminate tape chatter.

Tape 2 is used as a master tape in this chain to store all partial results. At the beginning of this storage, (WRITING TAPE 2) is printed on line. At the end (END OF WRITING TAPE 2) is printed on line. If the machine stops for any reason between these two points, all partial results are lost. If the machine stops at any other point in the program, and it is too late to restart, one can restart at any other time by saving Tape 2 until needed. Then one puts Tape 2 back on the

number two tape machine and restarts by following the restart instructions as given above.

The chain also contains the output routine. This routine writes the output as a column of floating point numbers with each number followed by four integers representing

$$D^2 = \sum_{i<j} a_{ij} X_i X_j^{*\prime}.$$

The a_{ij}'s are the floating point numbers, and the X_i is represented by the first two integers, whereas the $X_j^{*\prime}$ is represented by the last two integers. The format is (1X, E20.9, 4I3) . The trace is calculated and written in format (7H TRACE = E20.9) . The normalization constant is calculated and written in format (7H ANORM = E20.9) . The output routine only comes in use when the cycle number I reaches its largest value corresponding to the total number of Slater determinants in the wave function. When the cycle number is less than this value the chain ends by calling chain (1,3) into the memory of the machine. The process then starts over again with I increased by 1. Each cycle number I is printed on line so that the program can be followed and stopped at a safe place. We note that chain (4,3) is not called again, unless the job is a restart job.

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BIOGRAPHICAL SKETCH

Sidney James Fogel was born May 5, 1928, in Portland, Maine. He was educated in Portland public schools and was graduated from Portland High School in 1947, while serving with the United States Army in Japan.

Following his discharge from the army in 1947, he entered George Washington University night school where he studied for one semester. He returned to Maine following the death of his father and entered the University of Maine in September, 1949.

He was graduated in June, 1953, with a Bachelor of Science Degree (with distinction). He enrolled in the Graduate School of the University of Maine where he worked as a graduate assistant and later as a research assistant until June, 1955.

In September, 1955, he entered the University of Florida Graduate School for the study of fluorine chemistry. He later changed to the study of theoretical chemistry upon the formation of the Quantum Theory Project at the University. While at the University of Florida, he served as both graduate assistant and as research assistant.

Sidney James Fogel is married to the former Helen Marie Johnson. They have three children.

He is a member of the American Chemical Society and Tau Epsilon Phi.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1963

Dean, College of Arts and Sciences

Dean, Graduate School

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